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A SHORT MANUAL

OF

ANALYTICAL CHEMISTRY.

A SHORT MANUAL

OF

ANALYTICAL CHEMISTRY

Qualitative and Quantitative—Inorganic and Organic.

FOLLOWING THE COURSE OF INSTRUCTION GIVEN IN THE LABORATORIES OF THE

SOUTH LONDON SCHOOL OF PHARMACY.

BY

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PREFACE.

THE continued favour with which the book has been received in Great Britain has encouraged me to persevere in offering to American students a concise, and consequently low-priced, manual, designed to introduce them to the chief developments of analytical chemistry, from the simplest operations upwards, and including many organic questions generally overlooked in initiatory books. By working through it, a student will become familiar with a great variety of processes, and will then be in a position to use, with satisfaction, the more exhaustive treatises dealing with any special branch he may desire to follow. Originally written for the use of pharmaceutical students, it has, I hope, far passed the limits of a mere "examination" book, while not losing its value to them. Wherever the British processes were different from those of the U.S.P., they have been altered to suit that excellent and carefully compiled authority. In the first American edition the adaptation was done by the late Dr. Hamilton, and it was intended to place this one in the care of Dr. Bartley, of Brooklyn; but his engagements having prevented this well-known authority from getting through the work in time, I have been obliged to do it myself, and, although conscious that I have thus lost a valuable *collaborateur*, I trust I have suited American requirements.

J. M.

SOUTH LONDON SCHOOL OF PHARMACY,
325, KENNINGTON ROAD, LONDON, S.E.
July 1898.

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FOLLOWING THE COURSE OF INSTRUCTION GIVEN IN THE LABORATORIES OF THE

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BY

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PREFACE.

THE continued favour with which the book has been received in Great Britain has encouraged me to persevere in offering to American students a concise, and consequently low-priced, manual, designed to introduce them to the chief developments of analytical chemistry, from the simplest operations upwards, and including many organic questions generally overlooked in initiatory books. By working through it, a student will become familiar with a great variety of processes, and will then be in a position to use, with satisfaction, the more exhaustive treatises dealing with any special branch he may desire to follow. Originally written for the use of pharmaceutical students, it has, I hope, far passed the limits of a mere "examination" book, while not losing its value to them. Wherever the British processes were different from those of the U.S.P., they have been altered to suit that excellent and carefully compiled authority. In the first American edition the adaptation was done by the late Dr. Hamilton, and it was intended to place this one in the care of Dr. Bartley, of Brooklyn; but his engagements having prevented this well-known authority from getting through the work in time, I have been obliged to do it myself, and, although conscious that I have thus lost a valuable *collaborateur*, I trust I have suited American requirements.

J. M.

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325, KENNINGTON ROAD, LONDON, S.E.
July 1898.

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PART I.

QUALITATIVE ANALYSIS.

CHAPTER I.

THE PROCESSES EMPLOYED BY PRACTICAL CHEMISTS.

It is advisable that the student should understand the *raison d'être* of the chief processes he will be called upon to employ, before commencing in detail the study of Analysis.

I. SOLUTION.

This process consists in leaving a solid body in contact with a fluid until it dissolves, heat being occasionally used. Bodies which refuse to dissolve in any particular fluid are said to be **insoluble** in it; the liquid used is called the **solvent**, and sometimes the **menstruum**; a liquid having taken up all the solid matter possible is said to be **saturated**. A knowledge of the solubility of various substances in the chief menstrua, such as water, acids, alkalies, alcohol, ether, chloroform, and glycerine, is of the utmost importance, because we are thus enabled to separate one body from another; and, by attention to minute details, it is possible to part bodies which are soluble in the same menstruum, but in different degrees, the process being called *fractional solution*. In order to ascertain if any substance be soluble in any particular liquid, it is simply requisite to place it in the fluid, applying heat if necessary. A portion of the liquid is then poured off, and evaporated to dryness, when, if any of the solid be held in solution, it will remain as a visible residue. As a general rule, the higher the temperature to which a liquid is raised, the greater becomes its capacity for saturation. There are, however, exceptions to this rule—notably that of calcium oxide, which is less soluble in boiling water than in cold. Many bodies, during solution, absorb so much heat that any substance placed in the liquid has its temperature remarkably reduced. Sodium sulphate, dissolved in hydrochloric acid, forms in this manner a very efficient refrigerant when snow or ice is not obtainable.

II. LIXIVIATION AND EXTRACTION.

These processes include the digestion of a mixture of solids in a fluid, so as to dissolve the soluble portion. The solids, in the form of powder, are introduced into a vessel, and the water or other liquid having been added, the whole is well stirred. Remaining at rest until all the insoluble matter has subsided, the clear fluid, charged with all that was soluble in the mixture, is decanted, or drawn off by means of a **syphon.**

When a substance is to be extracted by means of a readily volatile solvent, such as ether or chloroform, the arrangement used is that known as **Soxhlet's apparatus.** This is illustrated in fig 1. A flask (A) is charged with the solvent. The substance (E) is put into a cartridge of filtering paper, and introduced into the Soxhlet tube (D); the latter is in turn connected with the upright condenser (C), through the jacket of which a stream of cold water is made to pass. Heat is now applied to the flask by a water bath, and the vapour of the ether, rising through B, condenses and drops on to the powder in the cartridge. When the instrument has become filled by the condensed solvent to the level of the top of F, it runs back into the flask, charged with the soluble matter that has been extracted. This process then repeats itself until the whole soluble portion has been extracted and transferred to the flask, which latter may then be attached to an ordinary condenser, and the solvent distilled off, leaving the soluble matters of the original powder in the flask. Resinous and sticky substances should be mixed with a little purified sand to prevent their clogging up the apparatus.

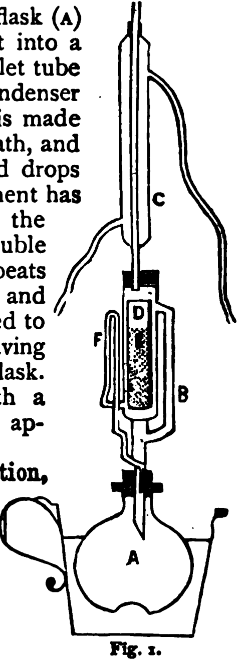

Fig. 1.

Another method of extraction is that known as **percolation,** a process much used in pharmacy. The apparatus employed is illustrated in fig. 2. The upper portion (A) is the percolator, in which the powder to be extracted is tightly packed and the solvent having been poured upon it, the whole is allowed to macerate for some time. The stopcock (C) being then opened, the fluid gradually filters into the receiver (B), and more solvent is then poured on until the soluble portion of the contents of the percolator has been entirely transferred to the receiver. The connecting tube is to prevent loss of volatile solvents.

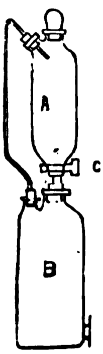

Fig. 2.

III. PRECIPITATION.

This process consists in mixing the solutions of two substances so as to form a third substance, which, being insoluble in the fluids employed, sinks to the bottom, and is called the **precipitate.** The clear liquid which remains after the precipitate has settled down is called the **supernatant liquid.**

When precipitates are totally insoluble in water (such as barium sulphate or argentic chloride), the operation is best conducted at a boiling heat, the high temperature causing the precipitate to aggregate, so that it subsides rapidly, and is less liable to pass through the pores of the filter. On the other hand, there are some precipitates which must never be heated, but be allowed to form slowly by standing in the cold for several hours. To this class belong ammonium-magnesium phosphate, and acid potassium tartrate. When it is desirable to cause precipitates to form quickly, resort may be had to stirring with a glass rod, so that it scrapes against the sides of the vessel.

In qualitative analysis precipitation is usually conducted in **test-tubes**

shown in fig. 3. These are kept in a stand (fig. 4) having holes for the reception of tubes actually in use, and also a row of pegs upon which freshly-washed tubes may be inverted to drain. Fig. 5 illustrates the appliance used to hold tubes when their contents are to be boiled, and fig. 6 shows the brush used for cleansing them.

Fig. 3.

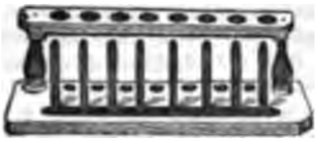
Fig. 4.

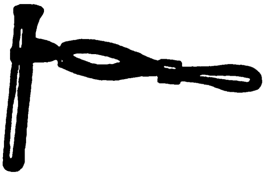
Fig. 5.

Fig. 6.

In quantitative analysis precipitation is generally performed in **beakers.** These are very thin tumblers made of glass, free from lead, and annealed so as to permit their use with boiling liquids without risk of fracture.

Precipitates are separated from the supernatant liquor by one of two methods. First:—

IV. DECANTATION,

which consists in allowing the precipitate to settle to the bottom, and pouring off the clear liquor. This is best done by the use of a glass rod held as shown in the illustration, fig. 7. Second:—

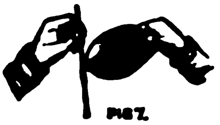
Fig. 7.

V. FILTRATION,

which consists in transferring the whole to a piece of folded filtering-paper or cloth placed in a funnel, so that the liquid passes through, while the precipitate remains. The liquor which has thus passed through the filter is called the **filtrate.**

Specially prepared circular papers for filtration are sold, and they have only to be folded to fit the funnel for which they are destined. The illustrations show, fig. 8 (A), the circle of paper, and (B) the same as folded for use, while fig. 9 represents the whole arrangement ready for use.

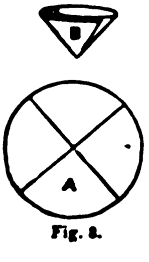

Fig. 8.

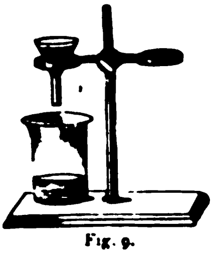
Fig. 9.

VI. DISTILLATION.

When a liquid is converted into vapour by the aid of heat, and the vapour is passed through a cooling apparatus, called a condenser, its latent heat is abstracted, and it is deposited as a liquid again. The process is called distillation. It is used to separate a volatile liquid from non-volatile substances. The liquid which passes over and is condensed in the receiver is called the **distillate**; while the non-volatile matter which remains in the retort is called the **residue**. Figure 10 shows the arrangement most commonly used in laboratories for small distillations. A is the **retort** in which the fluid is boiled, and B is called a **Liebig's condenser** (through the jacket of which a stream of water is caused to pass), and beneath the end of this is placed a vessel (C) for the reception of the distillate. By careful attention to their boiling points, various volatile fluids may thus be separated from each other. Suppose, for example, that we have a mixture of three substances boiling respectively at 80°, 100°, and 120°, and their separation is desired, we should introduce the mixture into a retort fitted with a thermometer, the bulb of which was placed just above the level of the fluid. The whole being then attached to the condenser, the heat would be gradually raised until the thermometer marked 80°, and that temperature would be steadily maintained as long as anything continued to collect in the receiver. When this ceased, the receiver would be changed, the temperature raised to 100°, and the distillation continued until the second liquid had ceased to pass over. The receiver being once more changed, the heat would be again raised, and maintained until the last liquid had been obtained as a distillate. This process is called **fractional distillation**.

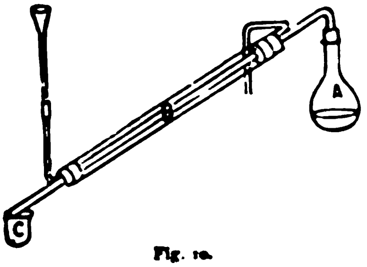

Fig. 10.

VII. SUBLIMATION.

When a solid is converted into vapour by heat, and again deposited unchanged in the solid form in a cooled vessel, it is said to have been subjected to sublimation. Sublimation is used to separate volatile from non-volatile solids, and is thus conducted:—The substance to be sublimed is thinly spread over the bottom of a shallow iron pan, covered with a sheet of bibulous paper perforated with numerous pin-holes, or with a piece of muslin. By means of a sand bath, the heat is slowly raised to the desired degree, when the vapour, passing through the strainer, condenses in a cap of wood or porcelain, lined with stout cartridge paper, previously placed over the heating-pan and kept cool. **Fractional sublimation** is often useful, and may be employed in a similar manner to fractional distillation.

VIII. FUSION

is the liquefaction of a solid by the aid of heat. It is usually carried out in a vessel called a crucible. For the purposes of analysis, fusion is generally conducted in porcelain, platinum, or silver crucibles, according to the nature of the substance under examination; but alkalies should be fused only in

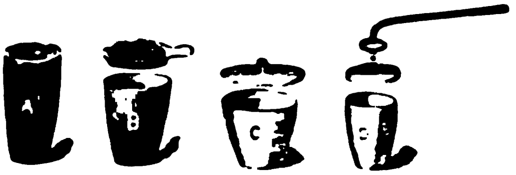

Fig. 11.

crucibles made of the latter metal. A peculiar kind of fusion, called **cupellation**, is resorted to in the assay of gold and silver bullion. The alloy to be assayed is wrapped in a piece of lead foil, and the whole is then heated in a little cup made of bone ash, called a **cupel**, when the lead, copper, etc., oxidise, fuse, and sink into the substance of the porous cupel, leaving the non-oxidisable metals as a metallic button, which may then be weighed. The illustration (fig. 11) shows a set of crucibles for fusion—A being of fire-clay; B, a platinum crucible; C, one of porcelain; and D, what is called *Rose's crucible*, for heating substances in a current of hydrogen when it is desired to prevent access of air, or to produce rapid reduction to the metallic state.

IX. EVAPORATION

consists in heating a liquid until the whole, or as much of it as may be required, passes off in vapour. A solution thus treated until it has wholly passed into vapour is said to be **evaporated to dryness**, and any solid substance remaining is called the **residue**.

Solutions containing organic or volatile bodies ought always to be evaporated on a water bath; that is, in a vessel exposed only to the heat of boiling water, in which the temperature must always be below 100° C. Evaporation may be conducted slowly, without raising the fluid to its boiling point, when it is called simply **vaporisation**; but when sufficient heat is applied, the evaporation takes place rapidly, and is accompanied by the disengagement of bubbles of vapour, and the fluid is then said to be in a state of **ebullition**. All liquids possess the continual desire, as it were, to pass into vapour, and the vapour formed endeavours to expand indefinitely; the pressure which is thus exerted by the vapour on the sides of the vessel containing it, is called its tension, and is measured by the height of the column of mercury it is able to sustain. The more the liquid is heated, the greater becomes its tendency to vaporise, and consequently the more powerful is the tension of its vapour; and when the latter is sufficiently marked to overcome the pressure exerted by the atmosphere and the cohesion of the liquid itself, ebullition takes place. The boiling point of a fluid is therefore *the temperature at which the tension of its vapour just exceeds the pressure of the superincumbent atmosphere.* If the pressure of the atmosphere be increased artificially, the boiling point of the liquid will rise in proportion. As steam under pressure can thus be obtained at high temperatures, it is made use of for the rapid evaporation of liquids on a large scale, by causing it to pass into a jacket surrounding the evaporating pan. The apparatus thus made use of is called a *steam bath*, the heat of which is officially understood to be about 110° C.

If water be boiled in a chemically clean glass vessel, and more particularly if a precipitate be suspended in the water, the boiling does not take place regularly, but the liquid becomes heated above its boiling point, and suddenly rushes into vapour in gusts. This is called by practical chemists "bumping," and may be prevented by putting in a few fragments of platinum foil, the air condensed on the surface of which, acting as a nucleus, aids in the regular disengagement of the vapour.

X. CRYSTALLISATION AND DIALYSIS.

Many substances when dissolved in a boiling liquid separate out, as soon as the fluid cools, in masses having a well-defined and symmetrical shape, bounded by plain surfaces and regular angles. These bodies are named **crystalline**; the deposited masses, **crystals**; and the remaining solution, the **mother liquor**. Substances which are not susceptible of crystallisation are called **amorphous** (*i.e.*, formless) bodies; while solids, such as glue and gums, which are soluble in water and yet not crystallisable, are named **colloids**. Crystallisation may also occur during solidification after fusion, and by the spontaneous evaporation of liquids holding crystalline substances in solution. All crystalline bodies invariably assume the same forms, and may thus be unmistakably recognised from each other. The process is also useful for purification, as at the moment of crystallisation impurities are rejected, and may be poured off with the mother liquor. Many circumstances affect the size of the crystals produced in any solution; as a rule, the more rapidly crystallisation takes place, the smaller are the crystals. An example of the extreme variation in the size of the crystals produced from the same solution may be seen in ferrous sulphate. When allowed to deposit slowly, we have the ordinary well-marked commercial crystals; but the same salt dissolved in boiling water, and the solution suddenly poured, with constant stirring, into spirit, gives granulated ferrous sulphate in crystals so minute that a lens is required to distinguish them. For the formation of large and well-defined crystals perfect rest is required, and it is often desirable to introduce pieces of wood or string so as to form nuclei on which the crystals collect. Good examples are seen in commercial crystallised sugar-of-milk and sugar-candy. Some bodies are capable of crystallising in two or more forms, and are called **di- tri- or poly-morphous**. Instances of this property may be seen in mercuric iodide and in sulphur.

When crystalline substances exist in a solution together with uncrystallisable colloid bodies, their mutual separation is effected by **dialysis**. This process consists in introducing the mixture into a glass vessel having a bottom made of vegetable parchment. This, called the **dialyser**, is floated in a large quantity of distilled water in a basin. At the expiration of several hours the crystalline bodies will have passed through the parchment, and will have become dissolved in the water in the basin, while the colloids remain in the dialyser. This process is sometimes employed for the separation of crystalline poison, like strychnine, from the contents of a stomach. The rapidity of the dialysis is greatly increased by causing a stream of water to pass through the outer basin, but of course this is only applicable where it is desired to retain the colloid body and not the crystalloid, as in the manufacture of the preparation known as *dialysed iron*. The apparatus used is shown in the illustration (fig. 12), in which A is the dialyser containing the mixture, while B contains the water into which the crystalline matter passes.

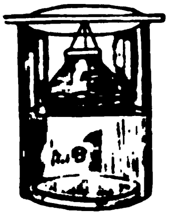

Fig. 12.

XI. ELECTROLYSIS

is the decomposition of bodies by means of electricity. The current of electricity is obtained from a **voltaic** or **galvanic cell** or **element**, and a combination of several cells is termed a **battery**. Bunsen's battery, which is very extensively used, consists of an outer cell or jar of glazed earthenware in which is placed a cylinder of zinc, an inner unglazed porous jar and a rod of carbon, both furnished with binding screws for attaching wires to them. The acids used are dilute sulphuric around the zinc, and strong nitric in contact with the carbon in the inner cell. The upper end of the carbon rod is called the *positive pole*, while that of the zinc plate is the *negative pole* of the cell. The ends of the wires leading from these are called electrodes; the wire from the carbon being the **anode**, and that from the zinc the **kathode**. On connecting these electrodes, a current of electricity passes along the wire which is assumed to flow from the positive to the negative pole. Any compound liquid which conducts electricity is called an **electrolyte**, and when the electrodes of a battery are immersed therein, it is decomposed into simpler bodies called "**ions**"; those thus formed at the anode being **anions**, and those liberated at the kathode being **kathions**. For instance, with a solution of HCl, Cl is given off at the anode, and H at the kathode, and the ions are the bodies thus directly liberated. Dealing with H_2SO_4, on the other hand, the first ions are H_2 at the kathode, and SO_4 at the anode; the latter, however, at once splitting up into O (given off) and SO_3, which re-forms H_2SO_4 with the water present.

Further reference to applications of electrolysis will be found in Chapter X., when the student arrives at quantitative analysis. It is also applied in a modified form in qualitative analysis to the separation of tin and antimony.

XII. PYROLOGY.

Under this name are included all processes of analysis depending for their action on the use of fire, or in other words, what are often called "*reactions in the dry way.*" The chief instruments used are the Bunsen burner and the blowpipe. The **blowpipe** is a tube with a narrow nozzle, by which a continuous current of air can be passed into an ordinary flame. The ordinary gas flame consists of three parts: (*a*) A non-luminous nucleus in the centre; (*b*) A luminous cone surrounding this nucleus; and (*c*) An outer and only slightly luminous cone surrounding the whole flame. The centre portion (*a*) contains unaltered gas, which cannot burn for want of oxygen, that necessary element being cut off by the outer zones. In the middle portion (*b*) the gas comes in contact with a certain amount of oxygen, but not enough to produce complete combustion; and therefore it is chiefly the hydrogen which burns here, the carbon separating and, by becoming intensely ignited, giving the light. In the outer zone (*c*) full combustion takes place, and the extreme of heat is arrived at, because chemical action is most intense. The outer flame therefore acts readily on oxidisable bodies, because of the high temperature and the unlimited supply of air, while the luminous zone tends to take away oxygen by reason of the excess of unburned carbon or hydrocarbons therein existing. For these reasons the former is called the **oxidising flame**, and the latter the **reducing flame**. The effect of blowing air across a flame is, first, to alter the shape of the flame, which is at once lengthened and narrowed; and, in the second place, to extend the sphere of combustion from the outer to the inner part (see fig. 12 *a*). As the latter circumstance causes an increase of the heat of the flame, and the former a concentration of that heat within narrower limits, it is easy to understand the great heat of the blow-pipe flame. The way of holding the blowpipe and the strength of the blast always depends upon whether the operator wants a *reducing* or an *oxidising* flame. The *reducing* flame is produced by keeping the jet of the blowpipe just on the border of a tolerably strong gas flame, and driving a moderate blast across it. The resulting mixture of the air with the gas is only imperfect, and there remains between the two parts of the flame a luminous and reducing zone, of which the hottest point lies somewhat beyond the apex of the inner cone. To produce the *oxidising* flame, the gas is lowered, the jet of the blowpipe pushed a little farther into the flame, and the strength of the current somewhat increased. This serves to effect an intimate mixture of the air and gas and an inner pointed, bluish cone, slightly luminous towards the apex, is formed, and surrounded by a thin, pointed, light-bluish, barely visible mantle. The hottest part of the flame is at the apex of the inner cone. Difficultly fusible bodies are exposed to this part to effect their

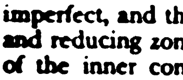

Fig. 12 a.

fusion; but bodies to be oxidised are held a little beyond the apex, that there may be no want of air for their combustion.

The *current* is produced by the cheek muscles alone, and not with the lungs. The way of doing this may be easily acquired by practising for some time to breathe quietly with puffed-up cheeks and with the blowpipe between the lips; with practice and patience the student will soon be able to produce an even and uninterrupted current.

The *supports* on which substances are exposed to the blowpipe flame are generally either wood charcoal, or platinum wire or foil.

Charcoal supports are used principally in the reduction of metallic oxides, etc., or in trying the fusibility of bodies. The substances to be operated upon are put into small conical cavities scooped out with a penknife. Metals that are volatile at the heat of the reducing flame evaporate wholly or in part upon the reduction of their oxides; in passing through the outer flame the metallic fumes are re-oxidised, and the oxide formed is deposited around the portion of matter upon the support. Such deposits are called incrustations. Many of these exhibit characteristic colours leading to the detection of the metals. Thoroughly burnt and smooth pieces of charcoal only should be selected for supports in blowpipe experiments, as imperfectly burnt and knotty pieces are apt to spirt and throw off the matter placed on them. The method of employing a charcoal support is shown in fig. 12 *b*.

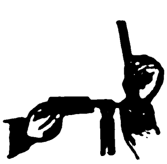

Fig. 12 *b*.

The great use of charcoal lies (1) in its low degree of conductivity; (2) its porosity, which causes it to absorb many fusible bodies and leave infusible ones upon its surface; and (3) its power of aiding the effects of the reducing flame.

Platinum wire and **foil** are used for supports in the oxidising flame, and the former is specially employed for trying the action of fluxes and the colour communicable to the blowpipe or Bunsen flame. The platinum wire, when employed for making beads of borax or other fluxes, should be about 3 to 4 inches long, with the end twisted into a small loop. The loop is then heated, and dipped while hot in the powdered borax, when it takes up a quantity, which is then heated till it fuses to a clear bead formed within the loop. When cold, this bead is moistened, dipped in the powder to be tested, and again exposed to the flame, and the effect noted. For trying the colour imparted to the flame by certain metals, the wire is first cleaned by boiling in dilute nitric acid and then holding it in the flame until no colour is obtained. The loop is then dipped in the solution to be tested, and held near the flame till the adhering drop has evaporated to dryness, and then heated in the mantle of the flame near the apex of the inner cone, and the effect observed.

Fig. 12 *c*.

The **Bunsen burner** consists of a tube having at its base a series of holes to admit air, and also a small gas delivery tube. By means of this contrivance the gas is mixed with air before it burns and more perfect oxidation, and consequently much greater heat, is secured. Looking attentively at the flame of a Bunsen burner, we distinguish in it an inner part and two mantles surrounding it. The inner part corresponds to the dark nucleus of the common gas flame, and contains the mixture of gas and air issuing from the burner. The mantle immediately surrounding the inner part contains still some unconsumed carbide of hydrogen; the outer mantle, which looks bluer and less luminous, consists of the last products of combustion. The Bunsen flame is illustrated in fig. 12 *c*. In it U O and L O are respectively the upper and lower oxidising flames, and U R and L R the upper and lower reducing ones, z f is the *zone of fusion* and is the hottest part, having a temperature (according to Bunsen) of 2,300° C. The spot where the reducing action is the most powerful and energetic lies immediately above the apex of the inner part of the flame. The Bunsen flame brings out the coloration which many substances impart to flames, and by which the qualitative analyst can detect many bodies, even though present in such minute quantities that all other means of analysis except the spectroscope fail to discover them. The subject of the coloration of flames will be discussed fully under each metal.

XIII. PREPARATION OF SULPHURETTED HYDROGEN.

This is done by acting upon ferrous sulphide with dilute sulphuric acid. The illustration (fig. 13) shows the apparatus. The ferrous sulphide, broken into lumps the size of a nut, is placed in the generating bottle (A), and dilute sulphuric acid is poured in by the funnel (C) in small quantities as required. B is a bottle containing distilled water, through which the gas passes to free it from any traces of acid mechanically carried over. Owing to the disagreeable odour, it is desirable to have special appliances, by means of which the evolution of the gas can be stopped as soon as it has done the work required. Such an apparatus for use in a large laboratory is that of Kipps (fig. 14); and one suitable for use by a single student is that of Van Babo fig. 15). Both illustrations sufficiently explain themselves.

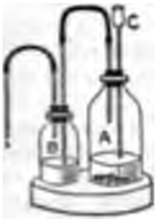

Fig. 13.

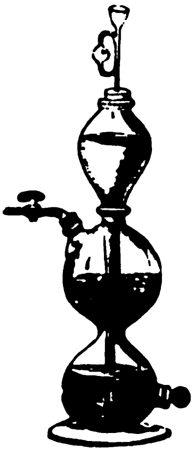

Fig. 14.

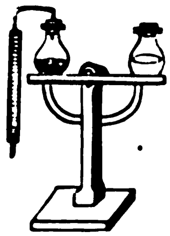

Fig. 15.

CHAPTER II.

DETECTION OF THE METALS.

FOR the purposes of qualitative analysis we employ certain chemicals, either in the solid or liquid state, which by producing given effects enable us to detect the existence of the substance searched for. These substances are always kept ready for use, and are called *reagents*. They are of three classes: 1st, **Group reagents**, which, by yielding a precipitate under certain conditions, prove the substance to be a member of a certain group of bodies; 2nd, **Separatory reagents**, by means of which the substance under examination is distinguished from the other members of the group; 3rd, **Confirmatory reagents**, by which the indications previously obtained are confirmed and rendered certain.

The Metals are divided into five groups, each of which has its group reagent, as follows:—

GROUP 1. Metals the chlorides of which, being insoluble in water, are precipitated from their solution by the addition of **hydrochloric acid**. They are **silver**, **mercurous mercury**, and **lead** (the latter in cold strong solutions only).

GROUP 2. Metals the sulphides of which, being insoluble in dilute hydrochloric acid, are precipitated from their solutions by the addition of **sulphuretted hydrogen** in the presence of hydrochloric acid. This group includes **mercury**, **lead**, **bismuth**, **copper**, **cadmium**, **antimony**, **tin**, **gold**, **platinum**, and the metalloid **arsenic**, and is divided into two sub-groups, as follows:—

A. Metals the sulphides of which are insoluble in both dilute hydrochloric acid and ammonium sulphide. The precipitated sulphides separated by sulphuretted hydrogen are therefore **insoluble**, after washing, in **ammonium sulphide**. They are **mercury**, **lead**, **bismuth**, **copper**, and **cadmium**.

B. Metals the sulphides of which, although insoluble in dilute acids, are dissolved by alkalies, and the precipitates from their solutions by **sulphuretted hydrogen** therefore dissolve in **ammonium sulphide**. They are **gold**, **platinum**, **tin**, **antimony**, and **arsenic**.

GROUP 3. Embraces those metals the sulphides of which are soluble in dilute acids, but are insoluble in alkalies, and which consequently, having escaped precipitation in Group 2, are now in turn precipitated by **ammonium sulphide**. They are **iron**, **nickel**, **cobalt**, **manganese**, and **zinc**. In this group are likewise included **aluminium**, **cerium**, and **chromium**, which are precipitated as **hydrates** by the alkalinity of the **ammonium sulphide**. **Magnesium** would also be precipitated as hydrate, but, as that would be inconvenient at this stage, its precipitation is prevented by the addition of **ammonium chloride**, in which its hydrate is soluble.

GROUP 4. Comprises metals the chlorides and sulphides of which, being soluble, escape precipitation in the former groups, but the carbonates of which, being insoluble in water, are now precipitated by **ammonium carbonate**. They are **barium, strontium**, and **calcium**. **Magnesium** is not precipitated as carbonate, owing to the presence of the **ammonium chloride** already added with the sulphide in Group 3.

GROUP 5. Includes metals the chlorides, sulphides, and carbonates of which, being soluble in **water** or in **ammonium chloride**, are not precipitated by any of the reagents already mentioned. They consist of **magnesium, lithium, potassium, sodium**, and **ammonium**.

As the analytical grouping of the metals is undoubtedly one which is most important to the student for practical purposes, we shall adhere to this arrangement in giving the methods for their detection.

GROUP I.

Metals precipitable as **chlorides** by the addition of hydrochloric acid to their solutions.

I. SILVER (Ag).

(*a*) *WET REACTIONS.*

(To be practised upon a solution of argentic nitrate—$AgNO_3$.)

1. **Hydrogen chloride** (*hydrochloric acid*)—**HCl** (*1st group reagent*)—or any soluble chloride gives a curdy white precipitate of argentic chloride—$AgCl$—insoluble in boiling nitric acid, but instantly soluble in ammonium hydrate. It is also soluble in KCN, $Na_2S_2O_3$, and in strong solutions of soluble chlorides.
2. **Potassium hydrate**—**KHO**—or **sodium hydrate**—**NaHO**—both produce a brownish precipitate of argentic oxide—Ag_2O—insoluble in excess. A similar effect is produced by the hydrates of barium, strontium, and calcium.
3. **Potassium chromate**—K_2CrO_4—gives a red precipitate of argentic chromate—Ag_2CrO_4—soluble in large excess of both nitric acid and ammonium hydrate; and therefore the solution should always be as neutral as possible.
4. **Hydrogen sulphide**—H_2S—and **ammonium hydrogen sulphide**—NH_4HS—both produce black argentic sulphide—Ag_2S—insoluble in excess, both soluble in strong boiling nitric acid.
5. **Potassium iodide**—**KI**—and **potassium bromide**—**KBr**—both produce curdy precipitates, the former yellow argentic iodide—AgI—insoluble in ammonium hydrate, and the latter argentic bromide—$AgBr$—dirty-white and slowly soluble in ammonium hydrate.
6. **Potassium cyanide**—**KCN**—gives a curdy-white precipitate of argentic cyanide—$AgCN$—readily soluble in excess, and also in boiling strong nitric acid.
7. Many organic salts, such as formates and tartrates, boiled with solutions of silver, precipitate the metal as a mirror on the tube.
8. Fragments of copper, zinc, iron, and tin, introduced into a solution of silver, all precipitate the metal.

(*b*) *DRY REACTION.*

(To be practised on argentic oxide—Ag_2O.)

Mixed with sodium carbonate and heated on charcoal before the blowpipe, a bead of silver is formed, hard, glistening, and soluble in nitric acid, yielding solution of argentic nitrate to which the wet tests may be applied.

II. MERCUROSUM $(Hg)^1$.

(*a*) *WET REACTIONS.*

(To be practised on a solution of mercurous nitrate—$Hg (NO_3)$ prepared by acting upon a globule of mercury with cold and dilute nitric acid.)

1. **HCl** (*1st group reagent*) gives a white precipitate of mercurous chloride,—$HgCl$—turned to black di-mercurous-ammonium chloride—NH_2Hg_2Cl—by ammonium hydrate. It is also insoluble in boiling water, but soluble in strong nitric acid, being converted into a mixture of mercuric chloride—$HgCl_2$—and mercuric nitrate—$Hg(NO_3)_2$.
2. **KHO** and **NaHO** both give black precipitates of mercurous oxide—Hg_2O—insoluble in excess.
3. **Ammonium hydrate**—NH_4HO—produces a black precipitate of dimercurous-ammonium nitrate—$NH_2Hg_2NO_3H_2O$—also insoluble in excess.
4. **Stannous chloride**—$SnCl_2$—boiled with the solution causes a grey precipitate of finely divided mercury, which, if allowed to settle, and then boiled with hydrochloric acid and some more stannous chloride, aggregates into a globule.
5. **KI** gives a green precipitate of mercurous iodide— HgI.

(*b*) *DRY REACTION.*

(To be tried upon mercurous iodide.)

Mercurous compounds when heated first break up into the corresponding mercuric salt and metallic mercury, and finally sublime unchanged.

III. LEAD (Pb).

(*a*) *WET REACTIONS.*

(To be practised on a solution of plumbic acetate—$Pb(C_2H_3O_2)_2$.)

1. **HCl** (*1st group reagent*) forms in cold strong solutions a white precipitate of plumbic chloride—$PbCl_2$—soluble in boiling water.
2. **H_2S** *after acidulation by* **HCl** (*2nd group reagent*) gives a black precipitate of plumbic sulphide—PbS—insoluble in ammonium sulphide. By treatment with boiling strong nitric acid it is decomposed, partly into plumbic nitrate, but chiefly into insoluble plumbic sulphate. It is entirely dissolved by hot dilute nitric acid with separation of sulphur.
3. **Hydrogen sulphate** (*sulphuric acid*)—H_2SO_4—gives a white precipitate of plumbic sulphate—$PbSO_4$—slightly soluble in water, but rendered entirely insoluble by the addition of a little alcohol. It is decomposed by boiling strong hydrochloric acid, and is also freely soluble in solutions of ammonium acetate or tartrate, containing an excess of ammonium hydrate.
4. **K_2CrO_4** gives a yellow precipitate of plumbic chromate—$PbCrO_4$—insoluble in acetic and very dilute nitric acids, but soluble in strong boiling nitric acid.
5. **KI** gives a yellow precipitate of plumbic iodide—PbI_2—soluble in 33 parts of boiling water, and crystallising out on cooling in golden scales.
6. **KHO** and **NaHO** both cause white precipitates of plumbic oxy-hydrate—$(PbO)_2\ Pb(HO)_2$—soluble in excess, forming potassium or sodium plumbates—K_2PbO_2 and Na_2PbO_2.
7. **NH_4HO** causes a white precipitate of a white basic nitrate—$Pb(NO_3HO)$—insoluble in excess.
8. **KCN** produces a white precipitate of plumbic cyanide—$Pb(CN)_2$—insoluble in excess, but soluble in dilute nitric acid.

9. **Alkaline Carbonates** cause a precipitate of $(PbCO_3)_2Pb(HO)_2$—"white lead"—insoluble in excess, and also in potassium cyanide.
10. Fragments of zinc or iron in the presence of a little acetic acid cause the separation of metallic lead in crystalline laminæ.

(*b*) *DRY REACTION.*

(To be practised on red lead—Pb_3O_4, or litharge—PbO.)

Heated on charcoal in the inner blowpipe flame, a bead of metallic lead is formed, which is soft and malleable, and soluble in dilute nitric acid. The solution thus obtained gives the wet tests for lead.

GROUP II.

Metals which are not affected by acidulation with hydrochloric acid, but are precipitated by passing sulphuretted hydrogen through the acidulated solution.

DIVISION A.

Metals which, when precipitated by sulphuretted hydrogen as above, yield sulphides insoluble in ammonium sulphide.

I. MERCURICUM (Hg)."

(*a*) *WET REACTIONS.*

(To be practised on a solution of mercuric chloride—$HgCl_2$.)

1. $\mathbf{H_2S}$ *after acidulation by* **HCl** (*2nd group reagent*) gives a black precipitate of mercuric sulphide—HgS—insoluble in ammonium sulphide and nitric acid, and only soluble in nitro-hydrochloric acid. Care must be taken that the sulphuretted hydrogen is passed really in excess, and that the whole is warmed gently, as unless this be done, the precipitate is not the true sulphide, but a yellowish-brown dimercuric sulpho-dichloride—Hg_2SCl_2. Although insoluble in any single acid, mercuric sulphide may be caused to dissolve in hydrochloric acid by the addition of a crystal of potassium chlorate.
2. **KHO** or **NaHO** both give a yellow precipitate of mercuric oxide—HgO—insoluble in excess.
3. $\mathbf{NH_4HO}$ produces a white precipitate of an insoluble mercuric-ammonium chloride—$(NH_2Hg)Cl$—also insoluble in excess.
4. **KI** yields a red precipitate of mercuric iodide, soluble in excess both of the precipitant and the mercuric salt.
5. $\mathbf{SnCl_2}$, boiled with a mercuric solution, first precipitates mercurous chloride, and then forms metallic mercury, as in the case of mercurosum compounds.
6. **Alkaline Carbonates** (except ammonium carbonate) produce an immediate reddish-brown precipitate of mercuric oxy-carbonate.
7. Fragments of Cu, Zn, or Fe precipitate metallic mercury in the presence of dilute hydrochloric acid.

(*b*) *DRY REACTION.*

(To be tried on mercuric oxide—HgO—and on "Ethiops mineral"—HgS.)

All compounds of mercury are volatile by heat; the oxide breaking up into oxygen and mercury, which sublimes, while the sulphide sublimes unaltered unless previously mixed with sodium carbonate or some reducing agent.

II. BISMUTH (Bi).

(*a*) *WET REACTIONS.*

(To be practised upon *bismuth subnitrate*, dissolved in water by the aid of the smallest possible quantity of nitric acid, and any excess of the latter carefully boiled off. This solution will then contain bismuth nitrate—$Bi(NO_3)_3$.

1. **H_2S** *after acidulation by* **HCl** (*2nd group reagent*) gives a black precipitate of bismuth sulphide—Bi_2S_3—insoluble in ammonium sulphide, but soluble in boiling nitric acid.
2. **H_2SO_4** gives no precipitate (distinction from lead).
3. **NH_4HO, KHO,** and **NaHO,** all give precipitates of white bismuthous hydrate $Bi(HO)_3$—insoluble in excess, and becoming converted into the yellow oxide—Bi_2O_3—on boiling.
4. **Water—H_2O**—in excess to a solution in which the free acid has been as much as possible driven off by boiling, gives a white precipitate of a basic salt of bismuth. This reaction is more delicate in the presence of hydrochloric than of nitric acid; and the precipitate, which is in this case bismuth oxy-chloride—$BiOCl$—is insoluble in tartaric acid (distinction from antimonious oxy-chloride).
5. **K_2CrO_4** yields a yellow precipitate of bismuth oxy-chromate—$Bi_2O_2CrO_4$—soluble in dilute nitric acid, but not in potassium hydrate (distinction from plumbic chromate).
6. **KI** gives brown bismuthous iodide, soluble in excess.
7. **Alkaline Carbonates** give white precipitates of bismuth oxy-carbonate, insoluble in excess.
8. Fragments of zinc added to a solution of bismuth cause a deposit of the metal as a dark grey powder.

(*b*) *DRY REACTION.*

(To be practised upon *bismuth subnitrate.*)

Mixed with sodium carbonate—Na_2CO_3—and heated on charcoal before the blowpipe, a hard bead of metallic bismuth is produced, and the surrounding charcoal is incrusted with a coating of oxide, deep orange-yellow while hot and pale yellow on cooling.

III. COPPER (Cu.)

(*a*) *WET REACTIONS.*

(To be practised with a solution of cupric sulphate—$CuSO_4$.)

1. **H_2S** *after acidulation with* **HCl** (*2nd group reagent*) forms a precipitate of brownish-black cupric sulphide—CuS—which is nearly insoluble in ammonium sulphide, but soluble in nitric acid. Its precipitation is prevented by the presence of potassium cyanide (distinction from cadmium). When long exposed to the air in a moist state, it oxidises to cupric sulphate and dissolves spontaneously.
2. **NH_4HO** causes a pale blue precipitate instantly soluble in excess, forming a deep blue solution of tetrammonio-cupric sulphate—$(NH_3)_4CuSO_4H_2O$.
3. **Potassium ferrocyanide—$K_4Fe(CN)_6$**—yields a chocolate-brown precipitate of cupric ferrocyanide—$Cu_2Fe(CN)_6$. This test is very delicate, and is not affected by the presence of a dilute acid, but does not take place in an alkaline liquid.

✓ 4. **KHO** or **NaHO** precipitates light-blue cupric hydrate—$Cu(HO)_2$—insoluble in excess, but turning to black cupric oxy-hydrate—$(CuO)_2Cu(HO)_2$—on boiling.

5. **Potassium sodium tartrate** (*Rochelle salt*)—$KNaC_4H_4O_6$—and **NaHO** added successively, the latter in excess, produce a deep blue liquid (Fehling's solution), which, when boiled with a solution of glucose (grape sugar) deposits brick-red cuprous oxide—Cu_2O.
6. The **Alkaline Carbonates** precipitate $Cu(HO)_2CuCO_3$.
7. Fragments of zinc or iron precipitate metallic copper from solutions acidulated with HCl.

(*b*) *DRY REACTIONS.*

(To be practised upon cupric oxide—CuO—or *verdigris*—$Cu_2O(C_2H_3O_2)_2$.)

1. Heated with Na_2CO_3 and KCN on charcoal, in the inner blowpipe flame, red scales of copper are formed.
2. Heated in the borax bead before the outer blowpipe flame, colours it green while hot and blue on cooling. By carefully moistening the bead with $SnCl_2$ and again heating, this time in the inner flame, a red colour is produced.

IV. CADMIUM (Cd).

(*a*) *WET REACTIONS.*

(To be practised with a solution of cadmium iodide—CdI_2.)

1. $\mathbf{H_2S}$ *after acidulation with* **HCl** (*2nd group reagent*) gives a yellow precipitate of cadmium sulphide—CdS—insoluble in ammonium sulphide, but soluble in boiling nitric acid. This precipitate does not form readily in presence of much acid; but its production is not hindered by the addition of potassium cyanide (distinction from copper).
2. $\mathbf{NH_4HO}$ produces a white precipitate of cadmium hydrate—$Cd(HO)_2$—soluble in excess.
3. **KHO** or **NaHO** both give precipitates of cadmium hydrate—$Cd(HO)_2$—insoluble in excess (distinction from zinc).
4. **Alkaline Carbonates** precipitate cadmium carbonate—$CdCO_3$—insoluble in excess.

(*b*) *DRY REACTION.*

(To be practised on cadmium carbonate—$CdCO_3$.)

Heated on charcoal before the blowpipe, a brownish incrustation of oxide is produced, owing to reduction of the metal and its subsequent volatilisation and oxidation by the outer flame.

DIVISION B.

Metals which are precipitated by sulphuretted hydrogen in the presence of hydrochloric acid, but yield sulphides which are soluble in ammonium sulphide.

I. ARSENIC (As).

(*a*) *WET REACTIONS.*

(To be practised with a solution of arsenious anhydride in boiling water slightly acidulated by hydrochloric acid.)

1. $\mathbf{H_2S}$, *after acidulation with* **HCl**, causes a yellow precipitate of arsenious sulphide—As_2S_3—soluble in ammonium sulphide, forming ammonium sulpharsenite—$(NH_4)_3AsS_3$—but insoluble in strong boiling hydrochloric acid (distinction from the sulphides of Sb and Sn). This precipitate is also soluble in cold solution of commercial carbonate of ammonia (distinction from the sulphides of Sb, Sn, Au, and Pt). Dried

and heated in a small tube with a mixture of Na_2CO_3 and KCN, it yields a mirror of arsenic. (Detects 1 part of As in 8000.)

2. Boiled with **KHO** *and a fragment of* **Zinc**, arseniuretted hydrogen—AsH_3—is evolved, which stains black a paper moistened with solution of argentic nitrate and held over the mouth of the tube during the ebullition (*Fleitmann's test*).
3. Boiled with $\frac{1}{7}$ of its bulk of **HCl** *and a slip of* **Copper**, a grey coating is deposited on the copper of cupric arsenide. On drying the copper carefully, cutting it into fragments, and heating in a wide tube, a crystalline sublimate of arsenious anhydride—As_2O_3—is obtained, which, when examined by a lens, is seen to be in octohedral crystals, and, when dissolved in water, gives a yellow precipitate of argentic arsenite—Ag_3AsO_3—with solution of ammonio-nitrate of silver (*Reinch's test*). (Detects 1 part As in 40,000.)

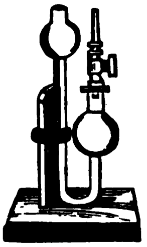

Fig. 16.

4. Placed in a gas bottle furnished with a jet (illustrated in the margin), together with dilute sulphuric or hydrochloric acid and a few fragments of zinc, arseniuretted hydrogen—AsH_3—is evolved, which may be lighted at the jet, and burns with a lambent flame, producing As_2O_3. If a piece of cold porcelain be held in the flame, dark spots of arsenic are obtained, readily volatile by heat and soluble in solution of chlorinated lime (*Marsh's test*). (Detects 1 part As in 200,000,000.)

Note.—For reactions of **arsenites** and **arseniates**, see Acid Radicals.

(*b*) *DRY REACTION.*

(To be practised on arsenious anhydride—As_2O_3.)

Heated in a small tube with Na_2CO_3 and KCN, a mirror of arsenic is produced, accompanied by a garlic-like odour. The same effect may be produced with black flux.

II. ANTIMONY (Sb).

(*a*) *WET REACTIONS.*

(To be practised with a solution of tartar emetic $(K(SbO)C_4H_4O_6)_2.H_2O$.)

1. H_2S, *after acidulation by* **HCl**, causes an orange precipitate of antimonious sulphide—Sb_2S_3—soluble in ammonium sulphide, forming ammonium sulphantimonite—$(NH_4)_3SbS_3$—also soluble in strong boiling hydrochloric acid, forming antimonious chloride—$SbCl_3$—but insoluble in cold solution of commercial carbonate of ammonia.
2. **KHO** *and* **NaHO** produce precipitates of antimonious oxide readily soluble in excess to form antimonites (K_3SbO_3 or Na_3SbO_3).
3. Acidulated with **HCl** and introduced into a **platinum dish** with a rod of **zinc** so held that it touches the platinum *outside* the liquid, a black stain of metallic antimony is produced closely adherent to the platinum. This stain is not dissolved by HCl (tin reduced in the same manne is granular and soluble in boiling HCl).
4. **Reinch's test** (see Arsenic) produces a black coating on the copper, which, when heated, forms an amorphous sublimate of Sb_2O_3 *close to the copper*, and insoluble in water, but dissolved by a solution of cream of tartar in which H_2S then produces the characteristic orange sulphide.
5. **Marsh's test** (see Arsenic) yields stains of antimony on the porcelain, not nearly so readily volatile by heat as in the case of arsenic, and not discharged by solution of chlorinated lime.

6. **Fleitmann's test** will not act with antimony at all (distinction from arsenic).

(*b*) *DRY REACTION.*

(To be practised on antimonious oxide—Sb_2O_3.)

Heated on charcoal with Na_2CO_3 and KCN before the blowpipe, a bead of metallic antimony is formed and copious white fumes of the oxide are produced.

III. TIN (Sn^{II} or Sn^{IV}).

(*a*) *WET REACTIONS.*

(To be practised with a solution of stannous chloride—$SnCl_2$—and one of stannic chloride—$SnCl_4$—prepared by warming the stannous solution with a little nitric acid.)

1. **H_2S**, *after acidulation with* **HCl**, produces a brown or yellow precipitate of SnS or SnS_2 respectively, both soluble in ammonium sulphide and in boiling hydrochloric acid.
2. **KHO** or **NaHO** both produce white precipitates of $Sn(HO)_2$ or $Sn(HO)_4$, soluble in excess, the former to produce *stannites* and the latter *stannates*. The stannous solution is, however, reprecipitable on boiling, while the stannic is not.
3. **NH_4HO** produces similar precipitates, very difficultly soluble in excess.
4. Acidulated by **HCl**, and introduced into a platinum dish with a rod of **zinc**, so held in the fluid that it touches the platinum *outside* the liquid, granules of metallic tin are deposited, soluble in boiling HCl, to form stannous chloride.
5. **$HgCl_2$** boiled with *stannous* salts deposits a grey precipitate of metallic mercury.

(*b*) *DRY REACTION.*

(To be practised on *putty powder*—SnO_2.)

Heated on charcoal with Na_2CO_3 before the blowpipe, a bead of metallic tin is produced, and a white incrustation of oxide is formed on the charcoal.

IV. GOLD (Au).

(*a*) *WET REACTIONS.*

(To be practised with a solution of auric chloride—$AuCl_3$.)

1. **H_2S** (*group reagent*) in the presence of HCl gives black auric sulphide —Au_2S_3. If the solution be hot, aurous sulphide—Au_2S—falls. Both are only soluble in nitro-hydrochloric acid, but they are soluble in ammonium sulphide when it is yellow.
2. **NH_4HO** precipitates reddish ammonium aurate, or *fulminating gold*—$Au_2(NH_3)_2O_3$—but KHO gives no result.
3. **Hydrogen oxalate** (*oxalic acid*)—**$H_2C_2O_4$** (or **Ferrous sulphate—$FeSO_4$**) —when boiled with an acid solution throws down Au. Reducing agents generally act thus. The liquid containing the metal may exhibit a blue, green, purple, or brown colour.
4. **$SnCl_2$** throws down a brownish or purplish precipitate known as "purple of Cassius," consisting of the mixed oxides of gold and tin.
5. **Zn, Cu, Fe, Pt**, or almost any metal, gives a precipitate of metallic Au in a finely divided state.

(*b*) *DRY REACTION.*

(To be practised on any gold salt.)

Heated on charcoal with Na_2CO_3, the metal is produced.

V. PLATINUM (Pt).

(*a*) *WET REACTIONS.*

(To be tested with a solution of platinic chloride—$PtCl_4$.)

1. **H_2S** (*2nd group reagent*) in presence of HCl gives a ***brown*** precipitate of platinic sulphide—PtS_2. This precipitate forms slowly, and is readily dissolved by yellow ammonium sulphide.
2. **Potassium chloride—KCl**—*in presence of* **HCl**, especially after addition of alcohol, produces a yellow crystalline precipitate of potassium platinic chloride—$PtCl_4(KCl)_2$—soluble to a moderate extent in water, but not in alcohol. Decomposition takes place when this is strongly heated, metallic Pt and KCl remaining.
3. **Ammonium chloride—NH_4Cl**—gives a precipitate of ammonium platinic chloride—$PtCl_4(NH_4Cl)_2$—which is almost identical in properties, but is more readily decomposed by heat, pure platinum remaining.
4. **Ln, Fe**, and several other metals decompose platinic salts with the production of the metal.

(*b*) *DRY REACTION.*

(To be practised upon potassium platinic chloride—$PtCl_4(KCl)_2$.)

Heat on charcoal, with or without Na_2CO_3, before the blowpipe. The metal is produced by reduction.

GROUP III.

Metals which escape precipitation by sulphuretted hydrogen in presence of hydrochloric acid, but which are precipitated by ammonium sulphide in the presence of ammonium hydrate, ammonium chloride having been previously added to prevent the precipitation of magnesium.

DIVISION A.

Metals which, *in the insured absence of organic matter*, are precipitated as hydrates by the addition of the ammonium chloride and ammonium hydrate only.

I. IRON (*Ferrous*, Fe; and *Ferric*, Fe_2).

(*a*) *WET REACTIONS.*

(To be practised successively on solutions of ferrous sulphate—$FeSO_4$—and ferric chloride—Fe_2Cl_6.)

1. **NH_4HO** *in the presence of* **NH_4Cl** (*group reagent*) yields either a dirty-green precipitate of ferrous hydrate—$Fe(HO)_2$—or a reddish-brown precipitate of ferric hydrate—$Fe_2(HO)_6$. The former is ***slightly*** soluble in excess, but the latter is insoluble, and it is therefore preferable always to warm the solution with a little nitric acid, to insure the raising of the iron to the ferric state, before adding the ammonium hydrate. The presence of organic acids, such as tartaric or citric,

prevents the occurrence of this reaction; and therefore, if any such admixture be suspected, the solution should first be evaporated to dryness, the residue heated to redness, and then dissolved in a little hydrochloric acid, heated with a drop or two of nitric acid, diluted, and lastly, the NH_4Cl and NH_4HO added and boiled.

2. **NH_4HS** added to a neutral or alkaline solution, produces a precipitate of ferrous sulphide—FeS—which is black (distinction from Al, Ce, Cr, Mn, and Zn), and readily soluble in cold diluted hydrochloric acid (distinction from the black sulphides of Ni and Co). This reaction takes place even in the presence of organic matter, and the precipitated sulphide, if exposed to the air, gradually oxidises to ferrous sulphate—$FeSO_4$—and disappears. It is insoluble in acetic acid (distinction from MnS).
3. **$K_4Fe(CN)_6$**, in a neutral or slightly acid solution, gives, with ferrous salts, a white precipitate (rapidly changing to pale blue) of Everett's salt—potassium ferrous ferrocyanide—$K_2Fe . Fe(CN)_6$—and with ferric salts, a dark blue precipitate of Prussian blue—ferric ferrocyanide $(Fe_2)_2(Fe(CN)_6)_3$. These precipitates are decomposed by alkalies, producing the hydrates of iron, and forming a ferrocyanide of the alkali in solution; but the addition of hydrochloric acid causes the re-formation of the original precipitate.
4. **Potassium ferricyanide—$K_6Fe_2(CN)_{12}$**—gives, with ferrous salts, in neutral or slightly acid solutions, a dark blue precipitate of Turnbull's blue—ferrous ferricyanide, $Fe_3Fe_2(CN)_{12}$—but with ferric salts it gives no precipitate, simply producing a brownish liquid. With alkalies, Turnbull's blue is decomposed, yielding black ferroso-ferric hydrate, and a ferricyanide of the alkali; but the addition of hydrochloric acid reproduces the original blue.
5. **Potassium thiocyanate** (*sulphocyanate*)—**$KCNS$**—gives no precipitate with ferrous salts, but with ferric compounds it yields a deep blood-red solution. This colour is not discharged by dilute hydrochloric acid (distinction from ferric acetate), but immediately bleached by solution of mercuric chloride (distinction from ferric meconate).
6. **KHO**, or **$NaHO$**, produces effects similar to those of ammonium hydrate.
7. **Disodium phosphate—Na_2HPO_4**—*in the presence of* **$NaC_2H_3O_2$** *or* **$NH_4C_2H_3O_2$**—gives a whitish gelatinous precipitate of ferrous or ferric phosphates—$Fe_3(PO_4)_2$ or $Fe_2(PO_4)_2$—insoluble in acetic acid, but soluble in hydrochloric acid. The previous addition of citric or tartaric acids prevents this reaction.
8. **Sodium acetate—$NaC_2H_3O_2$**—added in excess to *ferric* salts, produces a deep red solution of ferric acetate—$Fe_2(C_2H_3O_2)_6$—which on boiling deposits as a reddish-brown ferric oxyacetate—$Fe_3O(C_2H_3O_2)_4$. This precipitate dissolves slightly on cooling; but iron can be entirely precipitated in this form if the solution be instantly filtered while hot.
9. **Alkaline Carbonates**, added to a ferrous salt, precipitate white ferrous carbonate—$FeCO_3$—but with ferric salts throw down the reddish-brown ferric hydrate already described.

(*b*) *DRY REACTIONS.*

(To be practised on ferric oxide.)

1. **Heated on charcoal** before the inner blowpipe flame, a black magnetic powder is obtained, which is not the metal, but is ferroso-ferric oxide—Fe_3O_4.
2. **Heated in the borax bead** in the inner blowpipe flame, a bottle-green

colour is produced; but in the outer flame the bead is deep red while hot, and very pale yellow when cold.

II. CERIUM (Ce).

(*a*) *WET REACTIONS.*

(To be practised on cerous chloride—$CeCl_3$—prepared by boiling cerium oxalate with sodium hydrate, washing the insoluble cerous hydrate with boiling water, and dissolving it in the least possible excess of hydrochloric acid.)

1. **NH_4HO** *in the presence of* **NH_4Cl** (*group reagent*) gives a white precipitate of cerous hydrate—$Ce(HO)_6$—insoluble in excess.
2. **KHO** and **NaHO** give a similar precipitate, turning yellow on the addition of chlorine water.
3. **Ammonium oxalate** gives a white precipitate of cerous oxalate—$Ce_2(C_2O_4)_3 2H_2O$—insoluble in excess, and not readily dissolved even by hydrochloric acid. The presence of citric or tartaric acid does not interfere with this reaction.
4. **Potassium sulphate—K_2SO_4**—in a saturated solution causes the formation of white crystalline potassium cerium sulphate—$K_2SO_4Ce_2(SO_4)_3$—soluble in hot water.

(*b*) *DRY REACTIONS.*

(To be practised on cerium oxalate.)

1. Heated to redness in contact with the air, an orange red residue of ceric oxide—CeO_2—is obtained, difficultly soluble even in strong hydrochloric acid.
2. Heated in the borax bead, cerium behaves like iron in the outer flame, but the inner flame yields a colourless or opaque yellow bead.

III. ALUMINIUM (Al).

(*a*) *WET REACTIONS.*

(To be practised on a solution of *common alum.*)

1. **NH_4HO** *in presence of* **NH_4Cl** (*group reagent*) gives a gelatinous white precipitate of aluminic hydrate—$Al_2(HO)_6$. This precipitate is slightly soluble in a large excess of the precipitant, but separates completely on boiling.
2. **KHO** and **NaHO** both give a similar precipitate, soluble in excess, but reprecipitated by boiling with an excess of ammonium chloride, or by neutralising with hydrochloric acid and boiling with a slight excess of ammonium hydrate.
3. **Na_2HPO_4** *in the presence of* $NaC_2H_3O_2$ or $NH_4C_2H_3O_2$ gives a white precipitate of aluminic phosphate—$AlPO_4$—insoluble in hot acetic acid, but soluble in hydrochloric acid. The presence of citric or tartaric acids prevents the occurrence of this reaction.

(*b*) *DRY REACTION.*

(To be practised on *dried alum.*)

Heat strongly on charcoal before the blowpipe, when a strong incandescence is observed, and a white residue is left. Moisten this residue with a drop of solution of cobaltous nitrate—$Co(NO_3)_2$—and again heat strongly, when a blue mass is left. This test is not decisively characteristic, as other substances, such as zinc and earthy phosphates, show somewhat similar colours.

IV. CHROMIUM (Cr).

(*a*) *WET REACTIONS.*

(To be practised on a solution of potassium chromic chloride, prepared by dissolving potassium dichromate—$K_2Cr_2O_7$—in water, acidulating with hydrochloric acid, heating and dropping in alcohol till the solution turns green.)

1. **NH_4HO** *in the presence of* **NH_4Cl** (*group reagent*) precipitates green chromic hydrate—$Cr_2(HO)_6$—slightly soluble in excess, but entirely reprecipitated on boiling. The presence of citric or tartaric acid interferes with the completeness of this reaction.
2. **KHO**, or **NaHO**, gives similar precipitates, freely soluble in excess when cold, but entirely reprecipitable by continued boiling.
3. **Chlorinated soda**—**Na_2OCl_2**—or **Plumbic peroxide**—**PbO_2**—boiled with an alkaline solution of a chromium salt, produces a yellow solution of sodium chromate—Na_2CrO_4.
4. **$NaHPO_4$** *in the presence of* **$NaC_2H_3O_2$** or **$NH_4C_2H_3O_2$** throws down pale green chromic phosphate—$CrPO_4$—soluble when freshly precipitated in excess of hot acetic acid, and freely soluble in hydrochloric acid. The presence of organic acids prevents this reaction.

(*b*) *DRY REACTIONS.*

1. Heated in the borax bead in the inner blowpipe flame, a fine green colour is obtained.
2. Fused on platinum foil, with a mixture of $KNaCO_3$ and KNO_3, a yellow residue is obtained, consisting of chromates of the alkalies used. This mass is soluble in water, yielding a yellow solution turned deeper in colour by the addition of hydrochloric acid, owing to the formation of dichromates, and becoming green on warming and dropping in rectified spirit.

DIVISION B.

Metals the hydrates of which, being soluble in excess of ammonium hydrate in the presence of ammonium chloride, escape precipitation by that reagent, but are separated as insoluble sulphides by the addition of ammonium sulphide to the same liquid.

I. MANGANESE (Mn).

(*a*) *WET REACTIONS.*

(To be practised on a solution of potassium manganous chloride, prepared by heating a solution of potassium permanganate with hydrochloric acid, and dropping in alcohol until a colourless solution is obtained.)

1. **NH_4HS** *in the presence of* **NH_4Cl** *and* **NH_4HO** (*group reagent*) precipitates a flesh-coloured manganous sulphide—MnS—soluble in dilute and cold hydrochloric acid (distinction from the sulphides of Ni and Co). It is also soluble in acetic acid (distinction from zinc sulphide). This precipitate forms sometimes very slowly and only after gently warming. If a good excess of NH_4Cl has not been added, or if, after adding the excess of ammonium hydrate, the solution be exposed to the air, a portion of the manganese will sometimes precipitate spontaneously, as manganic dioxyhydrate—$Mn_2O.(HO)_2$—and be found with the iron, etc., in the first division of the third group. In this case its

presence will be easily made manifest during the fusion for chromium by the residue being green. It is therefore evident that small quantities of manganese cannot be perfectly separated from large quantities of iron by NH_4Cl and NH_4HO only.

2. **KHO** and **NaHO** both yield precipitates of manganous hydrate insoluble in excess, and converted by boiling into dark brown manganic dioxyhydrate—$Mn_2O_2(HO)_2$.
3. **NH_4HO** gives a similar precipitate, soluble in excess of ammonium chloride, but gradually depositing as $Mn_2O_2(HO)_2$ by exposure to the air. For this reason, if the presence of manganese be suspected, the addition of NH_4Cl and NH_4HO must be followed by instant filtration, and any cloudiness coming in the filtrate must be simply taken as indicating manganese, and disregarded.
4. **$K_4Fe(CN)_6$** gives a precipitate of manganous ferrocyanide—$Mn_2Fe(CN)_6$—very liable to be mistaken for the corresponding zinc compound.
5. Boiled with plumbic peroxide and nitric acid a violet colour is produced in the liquid, due to the formation of permanganic acid. (*Crum's test.*)

(*b*) *DRY REACTIONS.*

(To be practised upon manganese peroxide—MnO_2.)

1. Fused on platinum foil with KHO and a crystal of $KClO_3$, a green mass of potassium manganate is formed. This residue is soluble in water, yielding a green solution, turning purple on boiling, owing to the formation of potassium permanganate. The solution is rendered colourless by heating with hydrochloric acid and dropping in alcohol, the operation being accompanied by the odour of aldehyd.
2. Heated in the borax bead in the outer blowpipe flame, a colour is produced which is violet-red while hot and amethyst on cooling. The bead is rendered colourless by the reducing flame.

II. ZINC (Zn).

(*a*) *WET REACTIONS.*

(To be practised on zinc sulphate—$ZnSO_4$.)

1. **NH_4HS** *in the presence of* **NH_4Cl** *and* **NH_4HO** (*group reagent*) gives a white precipitate of zinc sulphide—ZnS—insoluble in acetic acid, but readily soluble in dilute hydrochloric acid.
2. **KHO**, **NaHO**, and **NH_4HO**, all give precipitates of gelatinous white zinc hydrate, soluble in excess to form zincates. The addition of sulphuretted hydrogen or ammonium sulphide reprecipitates the zinc as zinc sulphide—ZnS.
3. **$K_4Fe(CN)_6$** gives a gelatinous white precipitate of zinc ferrocyanide—$Zn_2Fe(CN)_6$—insoluble in dilute acids.
4. **Alkaline Carbonates** precipitate $ZnCO_2(Zn2HO)_2H_2O$—zinc hydratocarbonate—insoluble in excess of the carbonates of potassium and sodium, but soluble in that of ammonium. The latter solution, diluted and boiled, deposits the oxide.

(*b*) *DRY REACTIONS.*

(To be practised on zinc carbonate.)

1. Salts of zinc heated leave the oxide, yellow while hot, and white on cooling.

2. **Heated on charcoal** before the blowpipe an incrustation forms, yellow while hot, and white on cooling. Moisten with a drop of cobaltous nitrate—$Co(NO_3)_2$—and again heat it in the outer flame, when a fine green colour is produced.

III. NICKEL (Ni).

(*a*) *WET REACTIONS.*

(To be practised on a solution of nickelous sulphate—$NiSO_4$.)

1. **NH_4HS** *in the presence of* **NH_4Cl** *and* **NH_4HO** (*group reagent*) gives a black precipitate of nickelous sulphide—NiS—slightly soluble in excess, but entirely precipitated on boiling. It is not soluble in cold dilute hydrochloric or in acetic acid, but requires boiling with strong hydrochloric acid, and sometimes even the addition of a drop or two of nitric acid.
2. **KHO** or **NaHO** both give a green precipitate of nickelous hydrate—$Ni(HO)_2$—unaltered by boiling (distinction from cobalt).
3. **Potassium nitrite—KNO_2**—added to a neutral solution, followed by an excess of acetic acid, gives no precipitate (after standing some hours) on the addition of potassium acetate and rectified spirit (very useful separation from cobalt).
4. **KCN** in excess produces a greenish-yellow precipitate of nickelous cyanide—$Ni(CN)_2$—which quickly redissolves. On adding a drop of hydrochloric acid and boiling in a fume chamber, and repeating this till no more fumes of hydrocyanic acid come off, and then adding sodium hydrate, a precipitate of nickel hydrate is produced. It is better, although less convenient, to use a strong solution of chlorinated soda instead of HCl, when nickelic hydrate—$Ni(HO)_6$—is slowly precipitated (separation from Co, which gives no precipitate).
5. **Alkaline Carbonates** behave, so far as colour and solubility in excess are concerned, like their respective hydrates.

(*b*) *DRY REACTIONS.*

1. **Heated on charcoal** with Na_2CO_3 in the inner blowpipe flame, a grey metallic and magnetic powder is produced.
2. **Heated** in the borax bead in the outer blowpipe flame, red to violet-brown is produced while hot, and a yellowish to sherry-red when cold. These colours might be mistaken for those of iron; but on fusing a small fragment of potassium nitrate with the bead, its colour at once changes to blue or dark purple (distinction from Fe).

IV. COBALT (Co).

(*a*) *WET REACTIONS.*

(To be practised on a solution of cobaltous nitrate—$Co(NO_3)_2$.)

1. **NH_4HS** *in the presence of* **NH_4Cl** *and* **NH_4HO** (*group reagent*) gives a black precipitate of cobaltous sulphide—CoS—insoluble in acetic and cold dilute hydrochloric acid, and requiring to be boiled with the strongest HCl, often with the addition of a drop or two of nitric acid before solution is effected.
2. **KHO**, or **NaHO**, gives a blue precipitate, which rapidly changes on boiling to pink cobaltous hydrate—$Co(HO)_2$—(distinction from nickel).
3. **KCN** gives a light brown precipitate of cobaltous cyanide, rapidly soluble

in excess, but reprecipitated by excess of dilute hydrochloric acid. If, however, the HCl be added drop by drop just so long as it causes the evolution of hydrocyanic acid fumes on boiling,* soluble potassium cobalticyanide—$K_6CO_2(CN)_{12}$—results, which is not decomposed by hydrochloric acid; nor is any precipitate produced on adding excess of sodium hydrate or chlorinated soda (separation from nickel).

4. **Alkaline Carbonates** throw down basic carbonates, behaving like the respective hydrates.

(*b*) *DRY REACTIONS.*

1. Heated on charcoal with Na_2CO_3 in the inner blowpipe flame, the cobalt separates as a grey magnetic powder.
2. Heated in the borax bead, first in the *outer* and then in the *inner* flame, a fine blue colour is produced. It is an important distinction of cobalt from copper, manganese, etc., that *prolonged heating in the inner flame does not affect this blue.*

GROUP IV.

Metals the hydrates and sulphides of which, being soluble, are not precipitated by the addition of NH_4HO and NH_4HS in the presence of NH_4Cl, but separate as insoluble carbonates on the addition of ammonium carbonate to the same solution.

I. BARIUM (Ba).

(*a*) *WET REACTIONS.*

(To be practised on a solution of barium chloride—$BaCl_2$.)

1. **Ammonium carbonate**—$(NH_4)_2CO_3$—*in the presence of* NH_4Cl *and* NH_4HO (*group reagent*) produces a white precipitate of barium carbonate—$BaCO_3$—soluble with effervescence in dilute acetic acid.
2. H_2SO_4 and all **soluble Sulphates** give a white precipitate of barium sulphate—$BaSO_4$—insoluble in ammonium acetate or tartrate (distinction from $PbSO_4$) and also in boiling nitric acid.
3. K_2CrO_4 gives a yellow precipitate of barium chromate—$BaCrO_4$—insoluble in water and in dilute acetic acid, but soluble in hydrochloric acid (distinction from Sr and Ca).
4. $(NH_4)_2C_2O_4$ gives a white precipitate of barium oxalate—BaC_2O_4—not readily formed in the presence of much acetic acid.
5. Na_2HPO_4 gives a white precipitate of barium hydrogen phosphate—$BaHPO_4$—soluble in acetic acid, and to some extent in ammonium chloride.

(*b*) *DRY REACTION.*

(To be practised also on barium chloride.)

If a platinum wire be dipped first in hydrochloric acid and then in the salt, and held in the *inner* blowpipe or *Bunsen* flame, the outer flame is coloured yellowish-green.

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* This must be done in a fume chamber, as it is a highly poisonous operation if the fumes should happen to escape into the room.

II. STRONTIUM (Sr).

(*a*) *WET REACTIONS.*

(To be practised on strontium nitrate—$Sr(NO_3)_2$.)

1. **$(NH_4)_2CO_3$** *(group reagent) in the presence of* **NH_4Cl** *and* **NH_4HO** gives a white precipitate of strontium carbonate—$SrCO_3$—soluble in dilute acetic acid.
2. **H_2SO_4**, or a soluble sulphate (preferably calcium sulphate), yields a white precipitate of strontium sulphate—$SrSO_4$—which only separates completely from dilute solutions on allowing them to stand in a warm place for some hours. It is insoluble in a boiling strong solution of ammonium sulphate rendered alkaline by ammonium hydrate (distinction from calcium sulphate).
3. The other reactions are similar to those of calcium.

(*b*) *DRY REACTION.*

(To be also practised on $Sr(NO_3)_2$.)

A platinum wire moistened with hydrochloric acid, dipped in the substance and introduced into the *inner* blowpipe or *Bunsen* flame, colours the outer flame crimson.

III. CALCIUM (Ca).

(*a*) *WET REACTIONS.*

(To be practised on a solution of calcium chloride—$CaCl_2$.)

1. **$(NH_4)_2CO_3$** *in presence of* **NH_4Cl** *and* **NH_4HO** *(group reagent)* produces a white precipitate of calcium carbonate—$CaCO_3$—soluble in acetic acid and settling best on warming.
2. **$(NH_4)_2C_2O_4$** precipitates white calcium oxalate—CaC_2O_4—insoluble in acetic or oxalic acids, but soluble in hydrochloric acid.
3. **H_2SO_4** in strong solutions produces a precipitate of calcium sulphate—$CaSO_4$. Being slightly soluble in water, it does not form in dilute solutions, nor is it precipitated by a saturated solution of calcium sulphate (distinction from Ba and Sr). It is soluble in a boiling saturated solution of ammonium sulphate containing excess of ammonium hydrate, but quite insoluble in a mixture of two parts alcohol and one part water.
4. **Na_2HPO_4** produces a white precipitate of dicalcium phosphate—$CaHPO_4$—soluble in acetic acid.

(*b*) *DRY REACTION.*

(To be practised on calcium carbonate—$CaCO_3$.)

A platinum wire moistened with hydrochloric acid, dipped in the substance and held in the *inner* blowpipe or *Bunsen* flame, colours the outer flame yellowish-red. This reaction is masked by the presence of barium or strontium.

GROUP V.

Metals not precipitable either as sulphide, hydrate, or carbonate, including magnesium, the precipitation of which as hydrate or carbonate has been prevented by the presence of ammonium chloride.

I. MAGNESIUM (Mg).

(*a*) *WET REACTIONS.*

(To be practised on a solution of magnesium sulphate—$MgSO_4$.)

1. **Na_2HPO_4** *in the presence of* NH_4Cl *and* NH_4HO produces a white crystalline precipitate of ammonium magnesium phosphate—$MgNH_4PO_4$. It is slightly soluble in water, and scarcely at all in water containing ammonium hydrate, but entirely soluble in all acids. In very dilute solutions it only forms on cooling and shaking violently, or on rubbing the inside of the tube with a glass rod.
2. **$(NH_4)_2HAsO_4$** produces a similar precipitate of ammonium magnesium arseniate—$MgNH_4AsO_4$—possessing like features.
3. **KHO, $NaHO$,** and **NH_4HO** give precipitates of magnesium hydrate—$Mg(HO)_2$—insoluble in excess, but soluble in the presence of ammonium salts. The alkaline carbonates (except ammonium carbonate) precipitate magnesium carbonate, also soluble in ammonium salts.
4. **Calcium hydrate** (*lime water*)—**$Ca(HO)_2$**—and **Barium hydrate** (*baryta water*)—**$Ba(HO)_2$**—produce a similar effect. Either of these reagents is useful for the separation of magnesium from all the alkalies except ammonium. The solution, which must contain no ammonium salts, is treated with excess of either lime or baryta water. The precipitated magnesium hydrate is then filtered out and excess of ammonium carbonate added, which precipitates in turn the excess of Ca or Ba employed, and leaves K, Na, or Li in solution.

(*b*) *DRY REACTION.*

(To be practised on magnesium oxide.)

Heated on charcoal before the blowpipe, it becomes strongly incandescent, and leaves a white residue, which when moistened with a drop of solution of cobaltous nitrate—$Co(NO_3)_2$—and again heated, becomes rose-coloured. This test is not, however, infallible.

II. LITHIUM (Li).

(*a*) *WET REACTIONS.*

(To be practised on a solution of lithium chloride, prepared by dissolving lithium carbonate in dilute hydrochloric acid.)

1. **Na_2HPO_4** in strong solutions produces a white precipitate of lithium phosphate—$(Li_3PO_4)_2H_2O$—on boiling only (distinction from Mg). It is soluble in hydrochloric acid, and reprecipitated by boiling with ammonium hydrate.
2. **Na_2CO_3** and even NaHO, in very strong solutions, yield the carbonate and hydrate respectively.
3. **Platinic chloride—$PtCl_4$**—gives no precipitate (distinction from potassium).

b DRY REACTION.

(To be practised with lithium carbonate.)

A platinum wire, moistened with hydrochloric acid, dipped in the substance and held in the *inner* blowpipe or *Bunsen* flame, colours the outer flame *carmine red.* The presence of sodium disguises this reaction.

III. POTASSIUM (K).

WET REACTIONS.

(To be practised on solution of potassium carbonate treated with dilute HCl till effervescence ceases, forming potassium chloride—KCl.)

1. **$PtCl_4$**, in strong solutions, gives a yellow crystalline precipitate of potassium platino-chloride—$PtCl_4(KCl)_2$—soluble on great dilution, especially on warming, but insoluble in acids, alcohol, and ether.
2. **Hydrogen tartrate** (*tartaric acid*)—$H_2C_4H_4O_6$—throws down, from strong solutions only, a white crystalline precipitate of potassium hydrogen tartrate—$KHC_4H_4O_6$—soluble in much cold water, rather freely in hot water, readily in acids and in KHO or NaHO, and not formed unless the original solution be nearly neutral. Its separation is facilitated by stirring and shaking violently, in which case it settles quickly.
3. **Hydrogen silicofluoride** (*hydrofluosilicic acid*)—H_2SiF_6—yields white gelatinous potassium fluosilicate—K_2SiF_6—sparingly soluble in water.

DRY REACTION.

(To be practised on potassium carbonate—K_2CO_3.)

Dip a platinum wire, moistened with HCl, in the salt. Held in a *Bunsen* flame a *violet colour* is imparted. The masking effect of Na (*yellow*) is obviated by viewing the flame through cobalt glass.

IV. SODIUM (Na).

WET REACTIONS.

(To be tested with solution of sodium chloride—NaCl.)

1. **$K_2H_2Sb_2O_7$** (*potassium pyroantimoniate*, generally called *metantimoniate*) —gives a white granular precipitate of *sodium pyroantimoniate*— $Na_2H_2Sb_2O_7 6H_2O$—from strong solutions only, which must be neutral or alkaline. This precipitate is insoluble in alcohol.
2. **H_2SiF_6** gives a similar precipitate to that obtained with K salts in concentrated solutions only.

Sodium salts are, practically, all soluble in water, and there is no thoroughly trustworthy wet reaction which can be applied to detect small quantities. If we have a solution which gives no precipitate with any of the group reagents, but leaves, on evaporating, a non-volatile residue, capable of imparting a *strong yellow colour* to the *Bunsen* flame (**dry reaction**) we may infer with certainty the presence of sodium.

V. AMMONIUM (NH_4).

WET REACTIONS.

(To be tested with solution of ammonium chloride—NH_4Cl.)

1. **$PtCl_4$** produces a heavy yellow precipitate of ammonium platino-chloride— $PtCl_4(NH_4Cl)_2$—which, being rather soluble in water, is not formed in

dilute solutions, unless alcohol, in which it is insoluble, be added in considerable quantity. When ignited, pure spongy platinum is left. This precipitate may be distinguished from that with K salts by adding, after ignition, a little water and $AgNO_3$, when no white precipitate of AgCl is formed (the K salt leaves KCl on being strongly heated).

2. **$H_2C_4H_4O_6$** yields ammonium hydrogen tartrate—$(NH_4)HC_4H_4O_6$—almost identical with $KHC_4H_4O_6$ in its properties. On ignition, however, the latter gives a black residue, which turns moistened red litmus paper *blue* (K_2CO_3 and C), the former leaving pure C without reaction.
3. **NaHO** or **$Ca(HO)_2$** boiled with the solution causes the evolution of ammonia gas—NH_3. A glass rod dipped in HCl or $HC_2H_3O_2$ produces, when held over a mixture evolving NH_3, white clouds (solid NH_4 salts), and moist red litmus paper is turned blue.
4. **Nessler's Solution** (HgI_2 dissolved in KI and KHO added) gives a *yellow* or *brown colour*, or a *brown precipitate*, of dimercuric ammonium iodide —NHg_2IH_2O—with all NH_4 salts. This reaction is extremely delicate, and the estimation of NH_4 in water is founded upon it.

DRY REACTIONS.

Ammonium salts volatilise (1) with decomposition, leaving a fixed acid (*e.g.*, phosphate); (2) with decomposition, leaving no residue whatever (*e.g.*, sulphate, nitrate); (3) without decomposition, when they are said to ***sublime*** (*e.g.*, chloride, bromide, etc.).

CHAPTER III.

DETECTION AND SEPARATION OF ACID RADICALS.

I. HYDROFLUORIC ACID and FLUORIDES.

(The test for fluorides undernoted may be practised on fluor spar—CaF_2.)

Hydrofluoric Acid, or **Fluoric Acid**, is known—

1. By its **strongly acid reaction** and **corrosive power.**
2. By its **action upon glass**, from which it dissolves out silicic acid—SiO_2—thus roughening the surface and rendering it semi-opaque or translucent, and white; a colourless gas, silicic fluoride—SiF_4—passing off.

Fluorides are detected as follows:—

The mineral or salt is finely powdered, and introduced into a **leaden dish** with a little **sulphuric acid.** A piece of glass, previously prepared by coating its surface with wax, and etching a few letters on the waxed side with the point of a pin, is placed over the dish, waxed side down. A gentle heat is then applied, but not sufficient to melt the wax, and the operation continued for some time. The glass is then taken off, and the wax removed from it; when, if fluorine were present, the letters written on the waxed surface will be found engraved upon it by the action of the hydrofluoric acid.

2. CHLORINE, HYDROCHLORIC ACID, and CHLORIDES.

Free Chlorine—Cl_2—may be detected—

1. By its odour.
2. By turning paper dipped in solution of **potassium iodide** brown.
3. By bleaching a solution of **indigo** or **litmus.**

Hydrochloric Acid—HCl—may be recognised—

1. By its acidity and its giving off Cl_2 when heated with MnO_2.
2. By producing dense white fumes when a rod dipped in **ammonium hydrate** is held over the mouth of the bottle.
3. By giving a curdy white precipitate of argentic chloride with **argentic nitrate,** instantly soluble in **ammonium hydrate.**

Chlorides give the following reactions (to be practised with any soluble chloride, say NaCl):—

1. Heated with **sulphuric acid** they evolve white fumes of HCl.
2. Heated with H_2SO_4 and MnO_2 they evolve chlorine.
3. $AgNO_3$ *in the presence of* HNO_3 gives a white precipitate of argentic chloride—AgCl—insoluble in boiling nitric acid, but instantly soluble in dilute ammonium hydrate of a strength of 1 in 20.

4. The solid substance mixed with $\mathbf{K_2Cr_2O_7}$, and distilled with $\mathbf{H_2SO_4}$, yields chloro-chromic oxide—$CrCl_2O_2$—in red fumes which, when passed into dilute ammonium hydrate, colour it yellow, owing to the formation of ammonium chromate—$(NH_4)_2CrO_4$. The yellow should change readily to green on the addition of a few drops of sulphurous acid.

Insoluble Chlorides should be first boiled with **strong sodium hydrate** and the whole diluted and filtered. The chloride is then transferred to the sodium, and is to be searched for in the filtrate by acidulating with nitric acid and adding argentic nitrate, as above described.

3. HYPOCHLORITES.

(Practise on a solution of chlorinated lime—$Ca(ClO)_2CaCl_2$.)

Hypochlorites are all readily soluble in water, are contained in the so-called *chlorinated* compounds, and are recognised—

1. By having an odour of chlorine.
2. By giving a blue with **potassium iodide, starch paste,** and **acetic acid,** due to liberation of chlorine.

4. CHLORATES.

(To be practised on potassium chlorate—$KClO_3$.)

1. Heated on **charcoal,** they deflagrate.
2. Heated with **strong sulphuric acid,** they evolve chlorine peroxide—Cl_2O_4—which is yellow and explosive.
3. Their solutions yield no precipitate with **argentic nitrate**; but if a little of the solid be heated to redness, and the residue dissolved in water, a precipitate of argentic chloride may be obtained. The same reduction from chlorate to chloride may also be effected by adding zinc and dilute sulphuric acid to the solution.
4. Mixed with **KI** and **starch paste,** and acidulated with **acetic acid,** they give no blue (distinction from hypochlorites), but on adding **HCl** a blue is developed.

5. PERCHLORATES.

These are distinguished from chlorates—

1. By giving off perchloric acid—$HClO_4$—when heated with sulphuric acid, without explosion or evolution of chlorine peroxide.
2. Like chlorates, they require reduction to chlorides before giving a precipitate with argentic nitrate.

6. BROMINE, HYDROBROMIC ACID, and BROMIDES.

Bromine—$\mathbf{Br_2}$—is distinguished—

1. By its **appearance**—heavy, reddish-brown liquid, giving off reddish fumes of a very penetrating, unpleasant odour.
2. By turning **starch paste** orange.
3. When present in small quantity in solution, on adding a few drops of **chloroform** and shaking, an orange colour is imparted to that liquid, which sinks to the bottom of the aqueous solution.

Hydrobromic Acid—**HBr**—is known—

By its **acid reaction** and the production of fumes of bromine when heated with **strong sulphuric acid.**

Bromides are all soluble in water, except the silver, mercurous, and lead salts; they are detected by the following characters (to be practised on potassium bromide—KBr):—

1. Heated with **strong sulphuric acid**, they evolve red vapours of bromine.
2. A similar effect is produced by **sulphuric acid** and **metallic dioxides**, such as PbO_2, MnO_2.
3. Mixed with **starch paste**, and a few drops of **chlorine water** carefully added, they give an orange colour (starch bromide).
4. Mixed in a long tube with **chloroform**, and a few drops of **chlorine water** added, the whole, when shaken well together, leaves, on settling, a characteristic reddish-brown stratum at the bottom of the liquid in the tube, due to free bromine in the chloroform.
5. With **argentic nitrate** they give a dirty-white precipitate of argentic bromide, insoluble in nitric acid, slowly soluble in ammonium hydrate, but insoluble in dilute NH_4HO, of a strength of 1 in 20 (argentic chloride dissolves).
6. Distilled with **potassium dichromate** and **sulphuric acid**, red fumes are evolved, which give no colour when passed into **ammonium hydrate** (distinction from chlorides).

Insoluble Bromides should be first boiled with **NaHO**, as described under insoluble chlorides.

7. HYPOBROMITES.

These are very similar to hypochlorites, and react as follows:—

1. They decompose by heat, leaving a bromide;
2. On boiling with an alkali, a mixture of bromide and bromate results.

8. BROMATES.

These are recognised—

1. By deflagrating on charcoal, leaving the corresponding bromide.
2. By liberating bromine on the addition of dilute sulphurous acid.

9. IODINE, HYDRIODIC ACID, and IODIDES.

Iodine—I_2—may be recognised by its glistening black scales, its odour, the violet vapour on heating, and the production of blue iodide of starch on adding a solution to starch paste.

Hydriodic Acid—HI—in the gaseous state, is detected by the formation of a brown colour on paper moistened with chlorine water (blue if also dipped in starch paste) held over a tube from which it is being evolved.

Iodides are readily known by the following reactions (which may be practised on a solution of potassium iodide, KI):—

1. Heated with **strong sulphuric acid** they give a liberation of iodine with violet fumes.
2. **Mucilage of starch** and **chlorine water** or **strong nitric acid** (if not added too plentifully) produces **blue** iodide of starch, decomposed by heat, but re-formed on cooling; also bleached by excess of Cl.
3. **$AgNO_3$** gives a light yellow precipitate of argentic iodide—AgI. The precipitate, when freed from the supernatant liquid, does not dissolve in hot HNO_3, and is practically insoluble in ammonium hydrate, being thus distinguished from a chloride.

4. A *neutral* solution gives with one part of **cupric sulphate**—$CuSO_4$—and three parts of **ferrous sulphate**—$FeSO_4$—dissolved in a little water, a greyish precipitate of cuprous iodide—Cu_2I_2.
   The same precipitate is produced if **sulphurous acid**—H_2SO_3—be used with the cupric sulphate instead of ferrous sulphate.
5. **Palladious Chloride**—$PdCl_2$—or **palladious nitrate**—$Pd(NO_3)_2$—gives a black precipitate of palladious iodide—PdI_2—decomposed somewhat below the temperature of boiling mercury, iodine being evolved, and the metal left. This is a very expensive but efficient separation.
6. Mercuric chloride and plumbic nitrate give respectively red and yellow precipitates with soluble iodides.

10. IODATES.

(Practise on solution of potassium iodate—KIO_3.)

Iodates are known—

1. By giving, when heated with strong sulphuric acid, similar reactions to those obtained with chlorates.
2. By giving a blue colour with starch paste on the addition of sulphurous acid.
3. By giving a blue colour with starch paste on the addition of potassium iodide and tartaric acid.
4. By yielding a precipitate of ferric oxy-iodate on adding ferric chloride.

11. PERIODATES.

Periodates are distinguished—

1. By giving a precipitate with $BaCl_2$, in a neutral solution, which is not decomposed by digesting with ammonium carbonate and a little NH_4HO. Iodates leave barium carbonate, which when washed dissolves in acid with effervescence.
2. By adding $Hg(NO_3)_2$, and treating the yellowish precipitate with $SnCl_2$. It turns green, HgI_2 being produced.

12. WATER and HYDRATES.

Water is recognised—

1. By its absolute **neutrality** to test-paper.
2. By its evaporating without **residue**, **fumes**, or **odour** of any kind.
3. By its turning white anhydrous cupric sulphate blue.
4. By yielding **pure hydrogen** when it is boiled and the steam passed slowly over copper turnings heated to bright redness in an iron tube.
5. By its undergoing electrolysis when acidified, yielding **hydrogen** at the negative and **oxygen** at the positive electrode.

The **soluble Hydrates**, viz., KHO, $NaHO$, $LiHO$, $Ba(HO)_2$, $Sr(HO)_2$, and $Ca(HO)_2$ are known—

1. By being more or less soluble in cold water, yielding solutions which are strongly alkaline to test-paper.
2. By dissolving in **hydrochloric acid** without effervescence and without smell.
3. By giving a brownish-black precipitate of argentic oxide—Ag_2O—with **argentic nitrate**.

The **insoluble Hydrates** are recognised—

By giving off **steam** when heated in a dry test-tube, and leaving a residue which behaves like the corresponding oxide.

13. OXIDES.

All oxides are insoluble in water. Oxides of K, Na, Li, Ba, Sr, and Ca **unite with water** to form hydroxides, which dissolve with a greater or less degree of readiness and give the characters of the soluble hydrates already mentioned.

Normal Oxides can only be recognised by negative results, such as :—

1. Heated alone, they are not changed; except argentic oxide, which leaves the metal, and mercuric oxide, which volatilises and breaks up into the metal and oxygen.
2. They are **insoluble in water** (exceptions K, Na, etc., as above), but soluble in hydrochloric or nitric acid without effervescence and without smell.
3. After dissolving and removing the metal by H_2S or Na_2CO_3 as most convenient, no **acid radical** is found, other than that of the acid used to dissolve.
4. Boiled with strong **NaHO** and filtered, or fused with **KNaCO$_3$** and digested with water, the solution gives no reaction for any acid radical except the soluble hydrate or carbonate employed.

Peroxides, on account of their containing an excess of oxygen, differ from normal oxides (practise on MnO_2),—

1. By giving off **oxygen** when strongly heated.
2. By evolving **chlorine** when heated with **hydrochloric acid**.

14. SULPHUR, HYDROSULPHURIC ACID, and SULPHIDES.

Ordinary Sulphur—S_2 or S_6—is recognised—

1. By its **burning** entirely away with a pale blue flame, and evolving **sulphurous anhydride**.
2. By its insolubility in all ordinary menstrua, such as water, alcohol, and ether, but dissolving readily in carbon disulphide.
3. When slowly heated in a tube, it first melts, then thickens, then liquefies again, and finally boils, the vapour taking fire and forming sulphurous anhydride.

Precipitated Sulphur possesses the above characters, and is specially distinguished from ordinary sulphur by being quite **amorphous** under the microscope, while the latter is crystalline.

Hydrosulphuric Acid—H_2S (*sulphuretted hydrogen*)—is known—

1. By being a colourless gas with a **disgusting odour** of rotten eggs. It is inflammable, burning in the air to produce sulphurous acid.
2. By turning a piece of paper **black**, which has been moistened with solution of **plumbic acetate** and held over the mouth of the tube or jet from which it issues.

Normal Sulphides are divisible into five classes :—

1. Soluble in **water**, including the sulphides of K, Na, NH_4, Ca, Sr, Ba, and Mg.
2. Insoluble in water, but readily soluble in **dilute hydrochloric acid** including those of Fe, Mn, Zn.
3. Insoluble in dilute, but soluble in **strong boiling hydrochloric acid**, including the sulphides of Ni, Co, Sb, and Sn (PbS is also slightly affected, but separates on cooling, as chloride).
4. Insoluble in hydrochloric acid, but attacked by **strong heated nitric acid**, being converted wholly or partially into sulphates. These include the sulphides of Pb, Ag, Bi, Cu (arsenious sulphide is slowly affected).

5. Not dissolved by any single acid, but converted into a soluble sulphate by the action of **nitro-hydrochloric acid**, or hydrochloric acid and potassium chlorate; including those of Hg, As, Au, and Pt.

Sulphides soluble in water or in hydrochloric acid are recognised (practise on solution of Na_2S)—

1. By giving off sulphuretted hydrogen when heated with **HCl**.
2. Soluble sulphides give black and yellow precipitates, with solutions of **lead** and **cadmium** respectively.
3. Alkaline sulphides give a purple colour with **sodium nitroprusside** —$Na_2Fe(NO)C_5N_5$.

Sulphides insoluble in hydrochloric acid are best detected (practise on vermilion)—

1. Mix a little with **sodium carbonate** and **borax**, and heat on charcoal before the blowpipe. Remove the mass thus obtained, place it on a clean silver coin, and moisten with a drop of distilled water; when, owing to the formation during ignition of sodium sulphide—Na_2S,—a black stain of argentic sulphide—Ag_2S—will be produced.
2. By heating with **strong nitric** or **nitro-hydrochloric acid**, diluting the solution, and testing for a *sulphate* with **barium chloride** (see page 36).
3. By fusion with **$KNaCO_3$** and **KNO_3**, digesting the residue in water, filtering and testing the solution for a *sulphate*,—formed by the oxidising action of the potassium nitrate.

Polysulphides as commonly met with are those of the alkalies, and are soluble in water. They are known (practise on sulphuretted potash—K_2S_3)—

1. By the deep yellow or orange colour of their solutions.
2. By evolving sulphuretted hydrogen *accompanied by a deposit of sulphur* when treated with **hydrochloric** or dilute **sulphuric acids**.

The polysulphides which are insoluble in hydrochloric acid, such as iron pyrites, copper pyrites, etc., are best proved by fusion with potassium nitrate and carbonate and conversion into sulphate. They may, however, be recognised by heating with hydrochloric acid and zinc, when the excess of sulphur will pass off as H_2S, leaving the normal sulphide.

15. THIOSULPHATES (Hyposulphites).

(Practise on solution of sodium thiosulphate—$Na_2S_2O_3 5H_2O$.)

These salts, commonly known as hyposulphites, are usually soluble in water, and exhibit the following characters:—

1. With either dilute or strong **HCl** and **H_2SO_4**, they give off SO_2 and form a *yellow* deposit of S (*distinction from sulphides, polysulphides, and sulphites*).
1. **$AgNO_3$** gives no precipitate at first, owing to excess of a hyposulphite dissolving argentic hyposulphite—$Ag_2S_2O_3$—but on continuing the addition, this $Ag_2S_2O_3$ is precipitated of a *white* colour. The salt splits up spontaneously, becoming yellow, brown, and lastly black, and being changed completely into argentic sulphide—Ag_2S. The same decomposition of the precipitate occurs on substituting $HgNO_3$ or $Pb(NO_3)_2$ for $AgNO_3$; and in all three cases heat accelerates the action, and H_2SO_4 is the by-product.

3. **Fe_2Cl_6** produces a reddish-violet colour, gradually disappearing as $FeCl_2$ is formed. *(This colour is not produced by sulphites, and a somewhat similar tint produced by* Fe_2Cl_6 *in thiocyanates does not disappear.)*
4. **Na_2OCl_2** or **Cl_2** water converts hyposulphites into sulphates, even without applying heat.

16. SULPHUROUS ACID and SULPHITES.

Sulphurous Acid—H_2SO_3—is recognised in solution—

1. By its pungent odour of burning sulphur, due to evolution of SO_2. It combines directly with peroxides to form sulphates. For instance:—

$$PbO_2 + SO_2 = PbSO_4.$$

(This reaction is utilised in gas analysis, to separate SO_2 from a mixture.)

2. By adding **barium chloride** in excess, filtering out any precipitate of barium sulphate which may form (owing to the fact that all samples of the ordinary acid contain sulphuric acid), and then adding **chlorine water** and getting another copious white precipitate of barium sulphate, owing to the conversion of the sulphurous into sulphuric acid by the oxidising action of the chlorine water, thus:—

$$H_2SO_3 + BaCl_2 + Cl_2 + H_2O = BaSO_4 + 4HCl.$$

3. Treated with **zinc** and **hydrochloric acid**, it evolves sulphuretted hydrogen, thus:—

$$3Zn + 6HCl + H_2SO_3 = 3ZnCl_2 + H_2S + 3H_2O.$$

4. When a solution of **iodine** is dropped into the liquid, its colour is discharged, owing to its conversion into hydriodic acid by the hydrogen of the water, the oxygen of which passes at the same time to the sulphurous acid, forming sulphuric acid.

$$H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI.$$

Sulphites are known by the following characteristics (practise on solution of **sodium** sulphite—Na_2SO_3):—

1. All except the alkaline sulphites are sparingly soluble in water.
2. When heated with **sulphuric acid** they evolve sulphurous anhydride, *without deposit of sulphur.*
3. Acted on with **zinc** and **hydrochloric acid**, they evolve sulphuretted hydrogen, which blackens a piece of paper moistened with plumbic acetate and held over the mouth of the test-tube.
4. A salt of **silver, mercury,** or **lead** produces a precipitate which on heating turns dark, owing to the formation of a sulphide and free sulphuric acid.
5. By boiling with **barium chloride** and **chlorine water** or **nitric acid,** barium sulphate is produced, and precipitates.
6. **$K_2Cr_2O_7$** and **HCl** give a green coloration of *chromic sulphate* or *chloride.* This test is very delicate, but by itself is not conclusive, as any reducing agent acts similarly.

17. SULPHURIC ACID and SULPHATES.

Sulphuric Acid—H_2SO_4—is detected—

1. By its **appearance.** A heavy, oily, odourless, and nearly colourless liquid, powerfully acid and corrosive.
2. By its **charring effect.** This is made evident when the strong acid is dropped upon white paper, wood, etc., or when the dilute

acid is evaporated in a basin containing a little white sugar. The carbonisation is due to the power the acid has of abstracting the elements of water from organic bodies.

3. By liberating an explosive gas when dropped on a small fragment of **$KClO_3$**.

Sulphates are soluble in water, with the exception of *basic sulphates* (soluble in acids) and $BaSO_4$, $SrSO_4$, $CaSO_4$, and $PbSO_4$. (Ag_2SO_4 is only slightly soluble.) When it is necessary to analyse such sulphates as are insoluble in dilute acids, they are decomposed, either by boiling with potassium or sodium hydrates or by fusion with $KNaCO_3$ (the latter being preferable), and extracting the fused mass with water when the sulphate passes into solution. Sulphates are recognised by the following characters (practise on solution of magnesium sulphate):—

1. **$BaCl_2$** or **$Ba(NO_3)_2$** produces a white precipitate of barium sulphate —$BaSO_4$—insoluble in boiling water and boiling nitric acid. The addition of barium chloride to a strongly acid solution often causes the reagent to crystallise out, and this is then mistaken by the student for a true precipitate of sulphate; therefore the boiling water should always be employed.
2. The addition of a soluble salt of **lead** or **strontium** also causes the formation of insoluble sulphates; but these reactions are never used in practice, the barium chloride being at once the most delicate and serviceable reagent.
3. Heated with a little **Na_2CO_3** on charcoal in the inner blowpipe flame, sulphates are reduced to sulphides; and the residue, placed on a clean silver coin and moistened with water, leaves a black stain.

18. CARBON, CARBONIC ACID, and CARBONATES.

Carbon—**C_2**—is known—

1. By its black colour and by burning in the air and producing a gas which is odourless, so heavy that it can be poured from one vessel to another, and causes a white precipitate when passed into solution of **calcium hydrate**.
2. By its capability of removing many vegetable colouring matters from their solutions.

Carbonic Acid—**H_2CO_3**—is not known in the free state, as it splits up into **carbonic anhydride**—CO_2—and water on isolation. CO_2 is recognised—

1. By being odourless and giving white insoluble $CaCO_3$ (or $BaCO_3$) when passed into a solution of **$Ca(HO)_2$** (or $Ba(HO)_2$).
2. By turning blue litmus purple or wine-red, the original tint being restored by heat, the CO_2 escaping.

Carbonates are mostly insoluble in water, the alkaline carbonates alone dissolving. All carbonates give off CO_2 on ignition, except K_2CO_3 and Na_2CO_3. A white heat is needed to decompose $BaCO_3$ and $SrCO_3$. Most carbonates on heating to redness leave the oxide. Their recognition depends upon the following reactions (practise upon calcium carbonate)—

1. Effervescence with a solution of almost any acid (H_2S and HCN excepted), organic or inorganic, and giving off an odourless gas—CO_2.
2. When the gas given off is poured or passed into a solution of **calcium hydrate**, a white precipitate of $CaCO_3$ falls, soluble in excess of CO_2. When CO_2 is given off along with H_2S or SO_2,

either of these may be removed by passing through K_2CrO_4 and HCl, which is rendered green, and the unacted-upon CO_2 is allowed to pass into calcium hydrate solution as before, thus enabling us to detect a carbonate in the presence of a sulphide or sulphite.

3 **$HgCl_2$** gives a reddish-brown precipitate with the *carbonates* of of K, Na, and Li, and a white one with *bicarbonates* of the same metals.

4. Soluble carbonates give a white precipitate with cold solution of $MgSO_4$, while bicarbonates do not.

19. BORIC ACID and BORATES.

Boric (*or* **Boracic) Acid—H_3BO_3**—is distinguished as under:—

1. It is a white crystalline solid, giving off water on being heated, and leaving the *anhydride*—B_2O_3.
2. A solution in **alcohol** burns with a *green flame*.
3. When dissolved in hot water, and a piece of **turmeric paper** dipped in the solution, the yellow colour is unaffected; but upon drying the paper it becomes brownish-red, turned green on moistening with KHO.

All **borates** dissolve in dilute acids, but few in water, and when decomposed by hot acids, let fall crystalline boric acid on cooling, which answers to the above characters.

The presence of soluble **borates** is detected by the following tests (practise upon borax—$Na_2B_4O_7 10H_2O$:—

1. They give, on heating with **calcium chloride**, rendered slightly alkaline with ammonium hydrate, a white precipitate of calcium borate, soluble in acetic acid, and so distinguished from oxalate.
2. On rendering the solution *just acid* with **hydrochloric acid**, it reacts with **turmeric paper** as does H_3BO_3.
3. Besides these two tests, which are in themselves, taken together, quite conclusive, borates give a white precipitate with **argentic nitrate** soluble in **nitric acid**.
4. When a little of the solid borate is moistened with a drop of **sulphuric acid**, and **alcohol** is added, the green flame of H_3BO_3 is obtained on applying a light.

20. SILICIC ACID and SILICATES.

The acid **H_4SiO_4** is scarcely ever met with, and we have practically to deal with the anhydride—SiO_2—which is totally insoluble in water and dilute acids, the acid dissolving slightly in both. SiO_2 is characterised—

1. By its infusibility when heated.
2. By its insolubility in water, and all acids except HF.
3. By forming when heated with **H_2SO_4** and **CaF_2** in a leaden vessel, *gaseous silicic fluoride*—SiF_4—which deposits the acid—H_4SiO_4—and forms *hydro-fluosilicic* acid—H_2SiF_6—in contact with moisture.

Silicates are insoluble in water, except the alkaline silicates. Many of them do not dissolve in strong acids (a few are decomposed by hot H_2SO_4, but by no other acid), but all are split up by the action of gaseous hydrofluoric acid or a mixture of CaF_2 and H_2SO_4.

1. On adding **HCl** to an alkaline silicate, H_4SiO_4 falls as a gelatinous

—scarcely visible—precipitate, slightly soluble in water. On evaporating to dryness and heating to 140° or 150° C., the addition to the residue of a little HCl and water leaves the SiO_2 as a white gritty powder.

2. **NH_4Cl** precipitates H_4SiO_4 from an alkaline silicate.
3. Silicic anhydride is separated from all acid and basic radicals by fusing the finely powdered silicate with $KNaCO_3$ (*fusion mixture*), in a platinum crucible; adding dilute HCl to the residue till effervescence ceases, evaporating, and, when dry, heating to 140° or 150° C. On again treating this residue with water and HCl, SiO_2 alone remains insoluble.

21. HYDROFLUOSILICIC ACID (H_2SiF_6).

This acid is only known in solution.

1. It is very acid, and dissolves metals with the evolution of hydrogen, forming silico-fluorides which decompose by heat, leaving fluorides, and giving off silicon fluoride—SiF_4.
2. It gives off hydrofluoric acid when evaporated, and should not, therefore, be heated in glass vessels, as they would be etched.
3. The majority of silico-fluorides are soluble, the exceptions being K_2SiF_6, $BaSiF_6$, and Na_2SiF_6, which are insoluble, especially in presence of a little alcohol.
4. It does not precipitate strontium salts, even from strong solutions, but throws down $BaSiF_6$ on adding $BaCl_2$ and alcohol, as a *white translucent crystalline precipitate.*
5. Potassium salts throw down gelatinous K_2SiF_6.

22. NITROUS ACID AND NITRITES.

Nitrous Acid (so called commercially) is nitric acid containing nitrous anhydride. It is yellowish in colour, and evolves reddish fumes.

Nitrites are all soluble in water, the least so being argentic nitrite. They are known as follows (practise upon potassium nitrate which has been heated to dull redness or upon sodium nitrite—$NaNO_2$):—

1. They give red fumes when treated with **strong sulphuric acid.**
2. They give an instantaneous blue colour with **potassium iodide and starch paste** on the addition of a few drops of **dilute sulphuric acid.** The sulphuric acid liberates hydriodic acid from the iodide, and nitrous acid from the nitrite; the hydriodic acid is decomposed by the nitrous acid into iodine, water, and nitric oxide:—

$$2HNO_2 + 2HI = I_2 + 2H_2O + 2NO.$$

[*Nitrates*, it must be remembered, would give frequently a similar reaction after standing, through the possible reduction of some portion of their nitric acid to nitrous acid; so that unless the reaction appears instantly, and is confirmed by others, it is not safe to rely upon it as a test.]

3. They give a dark brown colour with **ferrous sulphate** *without the previous addition of sulphuric acid, as required by nitrates.*
4. **Potassium dichromate** in solution is converted into a green liquid by the addition of a nitrite and an acid. These two latter substances also reduce solution of auric chloride, forming a precipitate of the metal, possessing a dark colour.

23. NITRIC ACID and NITRATES.

Nitric Acid—**HNO_3**—is strongly acid and corrosive, fumes in tne air, and readily dissolves most metals. It may be at once recognised by the following characters:—

1. When poured on a piece of **copper foil**, and a piece of white paper held behind the test-tube, orange-red fumes of nitric peroxide —N_2O_4—are observed.
2. When dropped on a piece of **quill** in a basin, or evaporated in contact therewith, the quill is stained yellow, intensified to orange on adding an alkali, and not discharged by warming (*distinction from the corresponding stains produced by iodine and bromine*).
3. Dropped on a few crystals of **brucine**, a deep red colour is produced.

Nitrates are characterised by the following properties (practise upon solution of potassium nitrate—KNO_3):—

1. All nitrates are soluble in water, especially when slightly acidulated with nitric acid. The nitrates of the alkalies are only decomposed by a very high temperature, but nitrates of the heavy metals, such as copper, mercury, and lead, are readily decomposed by heat, leaving a residue of oxide. (Argentic nitrate leaves metallic silver.)
2. When heated with **sulphuric acid**, they evolve pungent fumes of nitric acid.
3. When heated with **sulphuric acid** and a piece of **copper wire**, red fumes of nitric peroxide are formed in the tube.
4. When mixed with a solution of **ferrous sulphate** in the presence of **sulphuric acid**, a black coloration is produced, due to the formation of nitrosyl ferrous sulphate. On heating, the colour disappears, and the *ferrous* is changed to the *ferric* sulphate.

Note.—There are two ways of applying this test:—

(*a*) Place a drop or two of the solution on a white porcelain slab or crucible lid, and having added a drop of strong sulphuric acid, put a small and clean crystal of the ferrous sulphate in the liquid, when a black ring will gradually form round the crystal.

(*b*) Place the solution in a tube, and having added some strong solution of ferrous sulphate, cautiously pour some strong sulphuric acid down the side of the tube, so that it sinks to the bottom by reason of its great gravity without mixing with the fluid. If nitric acid be present, a dark line will be formed at the junction of the two liquids.

5. Treated with **sulphuric acid**, and a few drops of **indigo sulphate** added, the blue colour of the latter is destroyed, being changed to yellow (not characteristic). $3C_{16}H_{10}N_2O_2$ (INDIGOTIN) + $4HNO_3 = 6C_8H_5NO_2$ (ISATIN) + $4NO + 2H_2O$.
6. The most delicate test for nitrates is, however, **phenol-sulphonic** (*sulpho-carbolic*) acid. This reagent is prepared by dissolving one part of carbolic acid in four parts of strong sulphuric acid, and then diluting with two parts of water. A few drops of the solution to be tested are evaporated to dryness on a porcelain crucible lid over the water bath, and while still over the bath a drop of the reagent is added, when a reddish colour is immediately produced, owing to the formation of nitro-phenol.

24. CYANOGEN, HYDROCYANIC ACID, and CYANIDES.

Cyanogen—(C_2N_2) or (Cy_2)—is a colourless gas, which is recognised—

1. By its odour of **bitter almonds**.
2. By its burning in the air with a **peach-blossom-coloured flame, producing** carbonic anhydride and nitrogen.
3. By forming **ammonium oxalate** when passed into water.

Hydrocyanic Acid—**HCN**—is volatile, soluble in water, and possesses a characteristic faint sickly odour of almonds. Its reddening action on **litmus** paper is very transient. Its tests are four in number, as follows:—

1. *The Silver Test.*—**Argentic nitrate** gives a curdy white **precipitate** of argentic cyanide. The precipitate is soluble in **ammonium** hydrate and in strong boiling nitric acid, but not in **dilute** nitric acid; nor does it blacken on exposure to the light.
2. *Scheele's Iron Test.*—An excess of solution of **potassium hydrate** is mixed with the solution. To this a mixture of a **ferrous and a ferric** salt is added, and the whole acidulated with **hydrochloric** acid. If hydrocyanic acid be present, *Prussian blue* **will be** formed.

The explanation of the test is as follows (according to Gerhardt's view):—

(1) The hydrocyanic acid and the potassium hydrate form potassium cyanide.
(2) The addition of the ferrous salt produces ferrous cyanide.
(3) This reacting with the excess of alkali forms potassium ferrocyanide.
(4) On the addition of the ferric salt, it is at first precipitated by the excess of **alkali**, as ferric hydrate, which on acidulation dissolves to ferric chloride, **forming** ferric ferrocyanide (Prussian blue).

(i.) $6HCN + 6KHO = 6KCN + 6H_2O.$
(ii.) $6KCN + 3FeCl_2 = 3Fe(CN)_2 + 6KCl.$
(iii.) $3Fe(CN)_2 + 4KHO = K_4Fe(CN)_6 + 2Fe(HO)_2.$
(iv.) $3K_4Fe(CN)_6 + 2Fe_2Cl_6 = (Fe_2)_2(Fe(CN)_6)_3 + 12\ KCl.$

Or the whole may be shown in one equation, thus:—

$$18KCN + 3FeCl_2 + 2Fe_2Cl_6 = (Fe_2)_2(Fe(CN)_6)_3 + 18\ KCl.$$

3. *The Sulphur Test.*—A few drops of **yellow ammonium sulphydrate** is added, and the whole is evaporated to dryness at a **very gentle** heat, with the addition of a drop of **ammonium hydrate**. A residue is thus obtained which (when cold) strikes a **blood**-red colour with **ferric chloride**, not dischargeable by **hydrochloric acid**, but at once bleached by solution of **mercuric chloride**.

This colour is due to the formation of ammonium thiocyanate (which takes place when an alkaline sulphide, containing excess of sulphur, is brought into contact with cyanogen)—

$$2HCN + (NH_4)_2S + S_2 = 2NH_4CNS + H_2S,$$

and subsequent production of red ferric sulphocyanide.

4. *Schönbein's Test.*—Filtering paper is soaked first in a 3 **per cent.** alcoholic solution of **guaiacum resin**, and then in a 2 **per cent.** solution of **cupric sulphate**, and exposed to the air. **When** this paper is either moistened with the suspected **solution or** exposed to its vapour, a blue colour is produced.

Cyanides are known (practise upon solution of potassium cyanide—KCN)—

1. By effervescing and giving off the odour of hydrocyanic acid **when** heated with **sulphuric acid**.
2. By answering to all the tests for hydrocyanic acid above **mentioned**.

Note.—In applying the silver test to a soluble cyanide, the reagent **must be added** in excess, as argentic cyanide is soluble in alkaline cyanides to form **double** cyanides of silver and the alkali used. Excess of argentic nitrate, however, decomposes these compounds, and forms insoluble argentic cyanide. The previous addition of a *slight* excess of dilute nitric acid ensures the immediate separation of the argentic cyanide, by preventing the reaction just referred to.

3. Insoluble cyanides yield cyanogen when heated *per se* in a small dry test-tube, the open end of which has been drawn out into a jet after the introduction of the cyanide. The application of a light to the jet gives the characteristic flame of cyanogen.

25. CYANIC ACID and CYANATES, CYANURIC ACID and FULMINIC ACID.

Cyanic Acid · **$HCNO$**—is characterised—

1. By being a colourless liquid, having a strong pungent odour, greatly resembling acetic acid, or very weak sulphurous acid, and forming ammonium bicarbonate on adding water.
2. By changing into a white solid *isomer* on keeping, heat being evolved, but no decomposition occurring.

Cyanates are known—

1. By giving, when moistened, a bicarbonate. (The potassium salt—$KCNO$—for instance forms potassium bicarbonate—$KHCO_3$.)
2. By producing urea when evaporated with an ammonium salt.

Cyanuric Acid is a polymeric modification of cyanic acid, which is recognised—

1. By being a crystalline solid, yielding cyanic acid on applying heat.
2. By not being decomposed by strong hot HNO_3 or H_2SO_4.

Fulminic Acid (intermediate between the two above acids) differs from both by the fearful explosibility of its salts.

26. THIOCYANATES (Sulphocyanates).

(Practise upon solution of potassium thiocyanate—$KCNS$).

Sulphocyanates are recognised—

1. By evolving hydrocyanic acid and depositing sulphur on heating with **sulphuric acid**.
2. By producing with **Fe_2Cl_6**, or any ferric salt, a blood-red solution of *ferric thiocyanate*—$Fe_2(CNS)_6$—not destroyed by **HCl** (*distinction from acetate*), but bleached by **mercuric chloride** (distinction from meconate).

27. FERROCYANIDES

(Practise upon solution of potassium ferrocyanide—$K_4Fe(CN)_6$.)

Ferrocyanides are mostly insoluble in water, except those of the metals of the first and second groups. They are characterised—

1. By giving off hydrocyanic acid and forming a deposit on heating with diluted **sulphuric acid**.
2. By giving with **$FeSO_4$** or any **ferrous salt** a white precipitate of potassium ferrous ferrocyanide—$K_2Fe(Fe(CN)_6)$—changing quickly to blue.
3. By yielding with **Fe_2Cl_6** or any **ferric salt** a dark blue precipitate of *ferric ferrocyanide*—$(Fe_2)(Fe(CN)_6)_3$—insoluble in HCl, but turned reddish-brown by KHO, which decomposes it into ferric hydrate and potassium ferrocyanide. The original blue is restored by adding HCl.
4. **Cupric salts** produce a reddish-brown precipitate of cupric ferrocyanide—$Cu_2Fe(CN)_6$—insoluble in acids, dissolved by NH_4HO but left unaltered on evaporating off the ammonia.

5. By precipitating white **plumbic** ferrocyanide from solutions of **lead salts.**
6. By yielding white mercuric ferrocyanide with a **mercuric salt.**
7. By giving a white gelatinous precipitate of **zinc ferrocyanide** on the addition of solutions of **zinc salts.**
8. By producing with **argentic nitrate**—$AgNO_3$—white gelatinous silver ferrocyanide, dissolved by NH_4HO on heating.

None of these precipitates can be produced in alkaline solutions; and they form best in slightly acid solutions.

28. FERRICYANIDES.

(Practise upon solution of potassium ferricyanide—$K_6Fe_2(CN)_{12}$.)

Most **ferricyanides** are insoluble, those of the alkalies and of the barium group being exceptions. They are recognised—

1. By yielding an odour of hydrocyanic acid, and a deposit on heating with diluted **sulphuric acid.**
2. By producing with $FeSO_4$ or any **ferrous** salt dark-tinted *Turnbull's blue*—$Fe_3Fe_2(CN)_{12}$—insoluble in acids, but forming $K_6Fe_2(CN)_{12}$ when boiled with KHO, and depositing dirty green $Fe(HO)_2$.
3. By producing no precipitate but a brownish coloration when added to Fe_2Cl_6 or any **ferric** salt in solution *(distinction from ferrocyanide)*.
4. By giving no precipitate in a **lead solution** *(another distinction from ferrocyanide)*.
5. By throwing down *mercurous ferricyanide* of a brownish-red colour from a **mercurous solution.**
6. By yielding with **argentic nitrate** solution an *orange* precipitate of argentic ferricyanide (*another distinction from ferrocyanide*).

29. HYPOPHOSPHITES.

(Practise upon solution of calcium hypophosphite—$Ca(PH_2O_2)_2$.)

All soluble except the silver salt. The following reactions serve for their detection:—

1. When heated in a solid state, they take fire, evolving phosphuretted hydrogen, and leaving a residue of pyrophosphate.

   Note.—This must be done on porcelain, as they destroy platinum foil.
2. With **argentic nitrate** they give a white precipitate, which turns brown owing to its reduction to metallic silver.
3. With **mercuric chloride** they yield, when slightly acidulated with **HCl**, a precipitate of calomel, which, on heating, turns dark, owing to a reduction to the metallic state.
4. After removal of the base, the free hypophosphorous acid, when boiled with solution of **cupric sulphate**, will give a deposit of metallic copper.
5. Treated with **ammonium molybdate**—$(NH_4)_2MoO_4$—they give a fine *blue* precipitate. As afterwards mentioned, *phosphates* give a *yellow*, and consequently when the solution contains both classes of salts the precipitate is *green*. This forms an excellent and rapid method of checking any commercial sample of hypophosphites.

They are distinguished from phosphites by not giving precipitates with neutral barium, or calcium chloride, or with plumbic acetate. In performing the 4th reaction, the base, if calcium, is removed by oxalic acid, if barium, by sulphuric acid, and if a heavy metal, by sulphuretted hydrogen.

20. PHOSPHOROUS ACID—H_3PO_3—and PHOSPHITES

are distinguished as follows:—

1. Heated on platinum foil, they burn. They are powerful reducing agents.
2. The only phosphites soluble in water are those of K, Na, and NH_4, but acetic acid dissolves all, except plumbic phosphite.
3. With zinc and sulphuric acid (nascent hydrogen) they yield phosphuretted hydrogen, burning with an emerald-green colour, and throwing down Ag_3P, as well as Ag from $AgNO_3$ in solution.
4. They give precipitates with neutral barium, and calcium chlorides, and also with plumbic acetate, which hypophosphites do not.
5. Heated with mercuric chloride or argentic nitrate, they yield a precipitate of metallic mercury or silver.

$$2HgCl_2 + 2H_3PO_3 + 2H_2O = 2H_3PO_4 + Hg_2 + 4HCl.$$

21. META- AND PYRO-PHOSPHORIC ACIDS AND THEIR SALTS.

Metaphosphoric Acid—HPO_3—is a glassy solid, not volatile by heat. It is freely soluble in cold water, and is converted by boiling into orthophosphoric acid. It is known by giving a white precipitate with ammonio-argentic nitrate, and by its power of coagulating albumen.

Metaphosphates are known by—

1. Giving no precipitate with ammonium chloride, ammonium hydrate, and magnesium sulphate, added successively.
2. Giving a white precipitate of argentic metaphosphate—$AgPO_3$—with argentic nitrate only in neutral solutions, and soluble both in nitric acid and ammonium hydrate.

Pyrophosphoric Acid—$H_4P_2O_7$—is also soluble in water and convertible by boiling into orthophosphoric acid. It gives a white precipitate with ammonio-argentic nitrate, but does not coagulate albumen. Pyrophosphates are insoluble in water, except those of the alkalies. Their tests are not very well defined, but they give—

1. A white precipitate of argentic pyrophosphate—$Ag_4P_2O_7$—with argentic nitrate in a neutral solution only, and soluble both in nitric acid and ammonium hydrate.
2. $(NH_4)_2MoO_4$ does not produce an immediate precipitate.

22. ORTHOPHOSPHORIC ACID and ORTHOPHOSPHATES.

Orthophosphoric acid—H_3PO_4—is a liquid with a strongly acid reaction, converted by heat first into pyro- and finally into meta-phosphoric acid, which remains as a glassy residue. It is—

1. Not volatile by a red heat.
2. It gives a yellow precipitate of **argentic phosphate—Ag_3PO_4**—when treated with **ammonio-argentic nitrate**, soluble both in nitric acid and ammonium hydrate.

Phosphates are as a rule insoluble in water, except the alkaline ones. They are readily soluble in dilute acids, and entirely reprecipitated on neutralising by an alkali or an alkaline carbonate. Calcium, strontium, and barium phosphates are only partly soluble in dilute sulphuric acid, being converted into a soluble phosphate and an insoluble sulphate of the metal. If the insoluble sulphate be filtered out, the addition of an alkali causes only a slight precipitate of a dimetallic phosphate, and a phosphate of the alkali used is left in solution; but it is only after the use of sulphuric acid that any phosphate thus remains dissolved.

Phosphates are detected as follows (practise on solution of disodium-phosphate—Na_2HPO_4)—

1. With **barium** or **calcium chloride** white precipitates are produced, soluble in acetic acid (*distinction from oxalates*) and all stronger acids.
2. With **argentic nitrate** a lemon-yellow precipitate of argentic phosphate forms, soluble both in nitric acid and ammonium hydrate.
3. With **ferric chloride** in the presence of **ammonium acetate** a white precipitate of ferric phosphate appears, insoluble in acetic acid.
4. With **magnesia mixture** phosphates yield a white crystalline precipitate, forming slowly in dilute solutions, consisting of ammonium-magnesium phosphate—$Mg(NH_4)PO_4 + 6H_2O$—soluble in acetic and all acids.
5. With solution of **ammonium molybdate** in **nitric acid** a yellow precipitate is produced, insoluble in nitric acid, but soluble in **ammonium hydrate**.
6. With **uranic nitrate**—$UrO_2(NO_3)_2$—phosphates yield a yellow precipitate of *uranic phosphate*, also insoluble in acetic acid.
7. With **mercurous** and **bismuthous nitrates** white precipitates are formed, the former soluble and the latter insoluble in nitric acid.
8. With any **soluble salt of lead** a white precipitate of plumbic phosphate is produced, soluble in nitric acid, but insoluble in acetic acid or ammonium hydrate.

Note.—Magnesia mixture is made by dissolving ordinary magnesium carbonate in a slight excess of dilute HCl, then adding to this solution ¼ of its bulk of strong NH_4HO, and finally stirring in solid NH_4Cl until the precipitate is dissolved.

33. ARSENIOUS ACID and ARSENITES.

Arsenious Acid—$\mathbf{H_3AsO_3}$—is not known in the free state; but its anhydride —As_2O_3—is commonly sold as arsenious acid, and when—

1. Dropped upon red-hot charcoal or coal, or heated in a dry tube with black flux (or a mixture of dry sodium carbonate and potassium cyanide), arsenic—$\mathbf{As_4}$—is set free, and volatilises with an odour of garlic, producing a steel-grey mirror on the sides of the tube.
2. Dissolved in water only, and **ammonio-argentic nitrate** added, a canary-yellow precipitate of argentic arsenite Ag_3AsO_3—is produced, soluble in excess of either NH_4HO or HNO_3.
3. A pure aqueous solution, mixed with **ammonio-cupric sulphate**, gives a bright-green cupric arsenite—*Scheele's green*—$CuHAsO_3$—also soluble in NH_4HO or in HNO_3.
4. Any solution yields all the reactions for **arsenic** (see page 15).

Arsenites behave peculiarly in many respects. Ammonium arsenite leaves arsenious acid on evaporating a solution, while potassium and sodium arsenites possess a degree of alkalinity which no excess of arsenious acid will disturb. Ba, Sr, and Ca form soluble hydrogen salts. All other arsenites are insoluble.

Neutral solutions of **arsenites** are possessed of the undermentioned distinctive peculiarities:—

1. $\mathbf{CuSO_4}$ throws down greenish cupric-hydrogen arsenite.
2. $\mathbf{AgNO_3}$ is transformed into yellow insoluble argentic arsenite.
3. $\mathbf{H_2S}$, *in the presence of hydrochloric acid*, gives a yellow precipitate of arsenious sulphide.
4. The solution gives the usual reactions for **arsenic** (see page 15).

34. ARSENIC ACID and ARSENIATES.

Arsenic Acid—H_3AsO_4—is known by the following characters:—

1. The crystals are deliquescent, white, and strongly acid. Heated, they leave a residue, which, on moistening with water, is also acid.
2. It is strongly corrosive and blisters the skin. It gives *brick red* Ag_3AsO_4 on adding **ammonio-argentic nitrate.**

Arseniates behave in every respect exactly like phosphates, except that they give a *brick-red* precipitate with **argentic nitrate**, instead of a *yellow*. Insoluble arseniates are best treated by boiling with NaHO, filtering, *exactly neutralising* the filtrate with dilute HNO_3, and then getting the brick-red precipitate with $AgNO_3$.

35. MANGANATES.

Manganates are unstable compounds, and only the alkaline salts dissolve in water, forming green solutions.

1. Soluble manganates decompose spontaneously, depositing MnO_2, the green colour changing to purple or reddish violet, owing to the formation of a permanganate,

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + 4KHO + MnO_2.$$

2. Dilute acids effect this change more rapidly, and the reaction is very delicate. The free hydrate is then replaced by a salt of the acid used.
3. Strong, heated H_2SO_4 acts as represented in this equation:-

$$K_2MnO_4 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + O_2.$$

4. Strong HCl causes the evolution of Cl_2. The other actions are similar to those of permanganates, but less energetic.

36. PERMANGANATES.

(Practise on solution of potassium permanganate—$KMnO_4$.)

Permanganates are known—

1. By the violet colour of their solutions, which is entirely bleached by **oxalic acid** or by heating with **hydrochloric acid** and dropping in **rectified spirit.**

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

2. By giving off oxygen on heating.
3. By giving off oxygen when heated with **sulphuric acid,** often with explosive violence.
4. By evolving chlorine when simply mixed with **hydrochloric acid.**
5. By getting the reactions for manganese after reducing with **HCl** and a few drops of **alcohol.**

37. CHROMIC ACID and CHROMATES.

Chromic Acid—H_2CrO_4—not being capable of isolation, is represented by its *anhydride*—CrO_3. This is a dark red crystalline solid, giving off oxygen when heated, and when mixed with an aqueous solution of *hydrogen peroxide*—(H_2O_2)—in ether a *deep blue* liquid results.

This test, for either CrO_3 or H_2O_2, is exceedingly delicate, the ethereal solution of perchromic acid separating from the water and thus concentrating the colour into a small bulk of ether.

Chromates of the alkalies are soluble, while those of the other metals are chiefly insoluble, but have brilliant yellow or red colours. They are very poisonous, and are detected as follows (practise on solution of K_2CrO_4 and $K_2Cr_2O_7$ respectively):—

1. **Soluble chromates** give a yellow precipitate with **plumbic acetate** or **barium chloride**, soluble in nitric acid, insoluble in acetic acid. The lead salt is darkened in colour by alkalies, and is freely soluble in excess of hot KHO.
2. With **argentic nitrate** a dark red precipitate, also soluble in nitric acid, and in NH_4HO, but not in acetic acid.
3. Boiled with **hydrochloric acid** and **alcohol**, or any reducing agent, they turn green, owing to the production of chromic chloride.
4. Treated with **sulphuretted hydrogen**, in the presence of **hydrochloric acid**, they turn green, and a deposit of sulphur takes place :—
$$2K_2Cr_2O_7 + 16HCl + 6H_2S = 2Cr_2Cl_6 + 4KCl + 3S_2 + 14H_2O.$$
5. Soluble chromates treated with an acid turn orange; and soluble dichromates, when treated with potassium hydrate, turn yellow. In this way they are mutually distinguished.
6. Heated with strong $\mathbf{H_2SO_4}$ they give off oxygen.
7. Treated with an excess of **sulphuric acid**, and shaken up with solution of hydrogen peroxide in ether, they give a gorgeous blue colour.

38. STANNIC ACID and STANNATES (Stannites ?).

This is thrown down by an alkaline hydrate from a stannic salt, and is also produced by the action of nitric acid upon tin.

Stannates are formed by the solution of the acid in an alkaline hydrate, and are detected in the examination for metals.

Stannites are said to be formed by the solution of stannous hydrates in an alkaline hydrate. They decompose on boiling with KHO, forming *stannates* and throwing down metallic tin.

39. ANTIMONIC ACID

Is produced by the action of nitric acid upon antimony as a white powder. Its presence is detected during the examination for metals.

40. FORMIC ACID and FORMATES.

Formic Acid—$\mathbf{HCHO_2}$—is the organic acid which contains the highest percentage of oxygen, and approaches most nearly in composition to the supposititious carbonic acid—H_2CO_3. It is a tolerably stable liquid, boiling at the same temperature as water. Formates are all soluble in water, and behave as follows :—

1. Heated to redness they decompose without blackening.
2. Heated with $\mathbf{H_2SO_4}$ they evolve CO, which, being free from CO_2, gives no effect when passed through *lime-water*, but burns with the usual pale blue flame. The reaction is—
$$HCHO_2 = CO + H_2O.$$
3. They readily reduce **argentic nitrate**, when boiled, metallic silver separating as a mirror on the tube.

41. ACETIC ACID and ACETATES.

Practise on sodium acetate—$NaC_2H_3O_2$.)

This acid is characterised by its odour of vinegar. The strong acid chars when heated with strong H_2SO_4.

Acetates are all soluble in water. They decompose at a red heat—if the heat rise gently and the mass be not alkaline—yielding *acetone*, and leaving a carbonate, oxide, or metal, according to the nature of the basic radical. When heated with alkalies *marsh gas*—CH_4—is evolved. The reaction is of this type:—

$$NaC_2H_3O_2 + NaHO = Na_2CO_3 + CH_4.$$

In the case of no alkaline hydrate or carbonate being present, the following is an example of the effect of heat on acetates:—

$$Ba(C_2H_3O_2)_2 = BaCO_3 + C_3H_6O \text{ (Acetone)}.$$

Acetates of easily reducible metals, such as copper, yield, when heated, a distillate of acetic acid, leaving a residue of the metal, or in some cases of oxide. The presence of **acetates** is analytically determined as follows:—

1. By evolving an odour of acetic acid when heated with **sulphuric acid.**
2. By a characteristic apple-like odour of acetic ether—$C_2H_5(C_2H_3O_2)$—which they evolve when heated with **sulphuric acid** and **alcohol.**
3. By the deep red colour which they produce with **neutral ferric chloride**—ferric acetate, $Fe_2(C_2H_3O_2)_6$—*dischargeable by both hydrochloric acid and mercuric chloride.*

42. VALERIANIC ACID and VALERIANATES.

Valerianic Acid—$HC_5H_9O_2$—is a liquid, which is—

Volatile, malodorous, colourless, and oily. It reddens test-paper, and dissolves in most *menstrua.*

The general characters of **Valerianates** are:—

1. A more or less strong odour of valerian root when warmed or moistened.
2. They give, when heated with **sulphuric acid,** an odour of valerian and a distillate which, on the addition of solution of **cupric acetate,** forms, after the lapse of some time, an oily precipitate; gradually solidifying, by the absorption of water, into a greenish-blue crystalline solid.

43. SULPHOVINATES (Ethyl sulphates).

These salts, derived from **ethyl hydrogen sulphate—$C_2H_5HSO_4$**—behave as follows:—

1. Heated with **strong sulphuric acid,** they evolve a faint ethereal odour.
2. They give no precipitate in the cold with **barium chloride**; but on boiling, a white precipitate of barium sulphate falls, and a smell of alcohol is perceived. The addition of a little solution of **barium hydrate** after the chloride and before boiling, facilitates the reaction; but in this case all metals precipitable by a fixed alkali must first, of course, be removed.
3. Heated to redness, they leave a sulphate of the metal.

4. Heated with **sulphuric acid** and an **acetate**, or with **strong acetic acid**, they evolve acetic ether with its characteristic odour of apples.

44. STEARIC ACID—$HC_{18}H_{35}O_2$—and STEARATES.

This acid is distinguished by the following characters:—

1. A white, odourless, fatty solid, melting by heat and soluble in absolute alcohol, the solution having an acid reaction.
2. Giving, when dissolved in **KHO** and the solution as nearly neutralised as possible, a white insoluble precipitate of plumbic stearate —$Pb(C_{18}H_{35}O_2)_2$—on the addition of **plumbic acetate**, which is insoluble in **ether** (distinction from plumbic oleate).

Stearates of the alkalies are alone soluble in water.

Any stearate heated with dilute **HCl** gives the free acid, which floats as an oily liquid, solidifying on cooling to a white mass. This test is applicable to the analysis of soap (*hard*, containing Na, or *soft*, in which K is present).

45. OLEIC ACID and OLEATES.

Oleic Acid—$HC_{18}H_{33}O_2$—is usually an oily liquid, but remains solid below 15° C. when crystallised from alcohol.

It does not dissolve in water, but is taken up by ether and by strong alcohol, the latter solution being acid in reaction.

Oleates of **K** and **Na** alone dissolve in water. Acid oleates are all liquid and soluble in cold absolute alcohol and ether.

1. They do not separate out from either of these solvents when a hot solution is cooled (*distinction from stearates and palmitates*).
2. *Plumbic oleate* is precipitable like plumbic stearate, but is separated and distinguished from it by dissolving in ether.

46. LACTIC ACID—$HC_3H_5O_3$—and LACTATES.

The pure strong acid resembles *glycerine* in appearance, liberates hydrogen on adding zinc, and on heating takes fire and burns away with a pale flame, gradually becoming luminous. It dissolves in ether. It gives pure CO when heated with sulphuric acid. Boiled with solution of potassium permanganate it gives the odour of aldehyd.

Lactates are not very soluble in water. They—

1. Are insoluble in ether.
2. *Argentic lactate*—$AgC_3H_5O_3$—when boiled gives a dark precipitate, which on subsidence leaves a *blue liquid*.
3. Strong solution of an alkaline lactate, when boiled with $HgNO_3$, deposits *crimson* or *pink* mercurous lactate $Hg_2(C_3H_5O_3)_2$.

47. OXALIC ACID and OXALATES.

(Practise on oxalic acid—$H_2C_2O_4$—and on "salts of sorrel.")

The acid is recognised—

1. By its colourless prismatic crystals, which are strongly acid, effloresce when exposed to dry air, and volatilise on heating with partial decomposition.
2. By the complete discharge it effects of the colour of a solution of **potassium permanganate** acidulated with **dilute H_2SO_4**.

3. By producing free **H_2SO_4** when added to solution of **$CuSO_4$**. (This is one of the very rare instances in which SO_4 is replaced by another acid radical and H_2SO_4 liberated.)
4. By giving the reactions of an oxalate.

Oxalates of the alkalies are soluble, the others insoluble, in water. Insoluble oxalates dissolve in hydrochloric, but not in acetic acid. They are known by—

1. Not charring when heated, but only turning faintly grey; followed by a sudden glow of incandescence, which runs through the mass.
2. Not charring when heated with **sulphuric acid,** but yielding CO and CO_2 with effervescence.
3. Not effervescing with cold **dilute sulphuric acid**; but at once liberating CO_2 with effervescence on the additon of a pinch of **manganese peroxide.**
4. With **calcium chloride** or **barium chloride** in a neutral or alkaline solution, they give a white precipitate of **calcium** or **barium oxalate,** *insoluble in acetic acid, but soluble in hydrochloric acid.*

(For separation of oxalates from tartrates, etc., see No. 78.)

48. SUCCINIC ACID—$H_2C_4H_4O_4$—and SUCCINATES.

This acid is a white crystalline solid. It is known –

1. By not charring with strong hot sulphuric acid.
2. By subliming in a tube open at both ends, in silky needles, *without giving off an irritating vapour* (distinction from benzoic acid).
3. By burning, when heated on platinum, with a blue smokeless flame.

Succinates are recognised as follows :—

1. With ferric chloride, a brownish-red precipitate of *ferric succinate*—$Fe_2(C_4H_4O_4)_3$—is formed.
2. With hydrochloric and sulphuric acids no precipitate is produced (*distinction from benzoates*). With *plumbic acetate*, a white precipitate of *plumbic succinate*, soluble in succinic acid, succinates, and plumbic acetate.
3. *Barium succinate* is soluble in hydrochloric acid, hence no effect results from the addition of succinic acid to barium chloride; but on the further addition of alcohol and ammonium hydrate, a white precipitate is formed (*another point of distinction from benzoates*).

49. MALIC ACID and MALATES.

Malic Acid – **$H_2C_4H_4O_5$**—is a colourless, crystalline, very deliquescent acid, freely soluble in water and alcohol. Acid **malates** are most stable. The characters are :—

1. Calcium chloride, added to a neutral solution of a malate, gives no precipitate. Alcohol, however, even if added in small quantity, throws down a white precipitate; and boiling aids the effect. If boiled with lime water, calcium malate dissolves. Calcium citrate is insoluble.
2. Strong H_2SO_4 gives no charring for some time (*a tartrate is carbonised in a few minutes*).
3. Amorphous *plumbic malate* fuses below 100° C. in water, but not in an air-bath.

50. TARTARIC ACID and TARTRATES.

(Practise upon the free acid and also upon "Rochelle salt.")

Tartaric Acid—**$H_2C_4H_4O_6$**—is a strong acid, soluble in water and spirit.

1. It forms usually oblique rhombic prismatic crystals, of an acid taste.
2. It is decomposed by heat, giving off the odour of *burnt sugar*, and leaving carbon. A similar effect is produced by warming with strong **H_2SO_4**, which blackens and carbonises it in a few minutes.
3. With **potassium acetate**—**$KC_2H_3O_2$**—it produces a white crystalline precipitate of *potassium hydrogen tartrate*—$KHC_4H_4O_6$—in either an aqueous or an alcoholic solution, soluble in much water, but not in spirit. Stirring or violent shaking promotes the formation of the salt.

The same compound is produced on adding any potassium salt, provided the liquid contain excess of free tartaric acid only.

Tartrates of the alkalies are mostly soluble; but the others are insoluble. The acid tartrates of K and (NH_4) are nearly insoluble. Tartrates are recognised by the following characters:—

1. Heated to dull redness they **char rapidly** and give off a smell of burnt sugar. The black residue contains the metal as carbonate if it be K, Na, Li, Ba, Sr, or Ca; but the tartrates of other metals usually leave the oxides, or more rarely (as in the case of $Ag_2C_4H_4O_6$) the metal.
2. Heated with **strong sulphuric acid**, they blacken *rapidly*, and give first a smell of burnt sugar, and afterwards evolve SO_2.
3. Neutral solutions (free from more than a trace of ammonium salts) give, on adding **calcium chloride**, a white precipitate of *calcium tartrate*, which, when freed from other salts by washing, dissolves readily in cold solution of potassium hydrate, but is again precipitated on boiling. The precipitate is somewhat soluble in NH_4Cl, but not in NH_4HO.
4. Mix a tartrate with **sodium carbonate**, and filter the slightly alkaline solution, so that the only metal present shall be sodium. If this clear solution, after *slight* acidulation with **acetic acid**, be mixed with **argentic nitrate**, the whole on heating nearly to boiling in a clean tube, deposits *a beautiful mirror of metallic silver* upon the test-tube employed.
5. A tartrate prevents the precipitation (more or less perfectly) of the salts of Pb, Bi, Cd, Cu, Pt, Fe_2, Mn, Ni, Co, Cr, and Zn, by an alkaline hydrate in excess, or by a phosphate.

51. CITRIC ACID and CITRATES.

(Practise upon the free acid and upon potassium citrate.)

Citric Acid—$H_3C_6H_5O_7$—is soluble in water and alcohol, but insoluble in pure ether. It entirely burns away when heated to redness in the air; blackens slowly when heated with strong sulphuric acid; and when neutralised by ammonium hydrate, and cooled, the solution gives no precipitate with calcium chloride until it has been boiled. Added to ferric, chromic, or aluminic salts in solution, it prevents their precipitation by ammonium hydrate.

Citrates exhibit the following characters:—

1. Heated alone, they **char slowly**, and evolve an odour of burnt sugar, but not so intense as that of a tartrate. At a dull red heat, the citrates of K, Na, Li, Ba, Sr, and Ca leave their carbonates; but those of most other metals leave the oxides. Argentic citrate leaves the metal.
2. Heated with **strong sulphuric acid**, they *slowly* blacken, and evolve a slight odour of burnt sugar.
3. Mixed in the cold with **calcium chloride**, in the presence of a slight excess of **ammonium hydrate**, they give no precipitate; but on boiling, calcium citrate—$Ca_3(C_6H_5O_7)_2$—separates as a white precipitate. If this precipitate be filtered hot, and washed with a little boiling water, it is found to be quite insoluble in cold solution of potassium hydrate, but readily soluble in neutral solution of cupric chloride.
4. Mixed with **argentic nitrate** and boiled, *no mirror* of metallic silver is produced.

52. MECONIC ACID and MECONATES.

Meconic Acid—$H_2C_7H_2O_7,3H_2O$—is a white powder, with a strongly acid reaction, soluble in water, alcohol, and ether, and giving the reaction for meconates.

Meconates communicate a red colour to ferric chloride solution. This colour is *not discharged by $HgCl_2$ nor by dilute HCl (distinction from a sulphocyanate and an acetate).*

53. CARBOLIC ACID (or Phenol)—C_6H_5HO—and CARBOLATES (Phenates).

The qualities of this body are very distinctive.

1. It is a colourless, crystalline solid, melting at not lower than 33° C., and not volatile at 100° C., having the odour and taste of creasote, being very poisonous, and not reddening blue litmus paper.
2. The crystals deliquesce readily, forming a liquid which does not mix freely with water, but is soluble in all proportions in alcohol, ether, and glycerine.
3. Mixed with **HCl** and exposed to the air on a strip of deal, it becomes greenish blue.
4. It coagulates *albumen.* It does not rotate polarised light.
5. Saturated with **ammonia gas**—NH_3—and heated in a closed tube, *aniline* is formed:—
$$C_6H_5HO + NH_3 = C_6H_5H_2N + H_2O.$$
6. It does not decompose carbonates.
7. NH_4HO and $CaOCl_2$, or Na_2OCl_2, produce a blue liquid, turned red by acids.
8. It unites directly with strong H_2SO_4 to form phenol-sulphonic (or *sulpho-carbolic*) acid.
9. With **bromine water** it gives a white precipitate of tribromophenol —$C_6H_3Br_3O$.

Carbolates give the following reactions:—

1. When heated alone, they evolve the odour of carbolic acid and decompose.
2. Heated with **strong sulphuric** acid they also smell of carbolic acid.
3. **Ferric chloride** causes a reddish-violet colour.

Sulpho-Carbolates behave similarly, but, after fusion with KNO_3 and redissolving the residue in diluted **HCl**, they also give the reactions of a sulphate with barium chloride.

54. BENZOIC ACID and BENZOATES.

Benzoic Acid—$HC_7H_5O_2$—is of characteristic appearance, being usually seen in light, feathery, flexible, nearly colourless crystalline plates or needles, and containing a trace of an agreeable volatile oil, unless it is the artificial acid prepared from naphthalene, when it is odourless.

1. It is only slightly soluble in water, but dissolves in three parts of alcohol, and in solutions of soluble hydrates.
2. Heated in the air, it burns with a luminous smoky flame; and when made hot in a tube open at both ends, sublimes in needles, giving off an *irritating vapour.*

Benzoates possess the following general qualities:—

1. Heated with **sulphuric acid** they evolve the odour of benzoic acid, and darken.
2. **Ferric chloride**, in a solution made *slightly* alkaline by **ammonium hydrate**, gives a reddish-white precipitate—ferric benzoate—

$Fe_2(C_7H_5O_2)_6$—soluble in acids (*benzoic* included) If this precipitate be now filtered out and digested in ammonium **hydrate**, it is decomposed into a precipitate of ferric hydrate, and a solution of ammonium benzoate, which is separated by filtration and treated as in 3.

3. Strong hot solutions of benzoates yield crystals of *benzoic acid* when **hydrochloric acid** is added and the solution allowed to cool.

55. SALICYLIC ACID ($HC_7H_5O_3$).

This acid occurs in prisms, when crystallised from a solution in alcohol in which it is readily soluble. It is freely dissolved by hot water, but not readily by cold, requiring 1,800 parts of the latter to completely dissolve it.

1. Its aqueous solution gives with **ferric chloride** a *deep violet coloration*. The compounds with methyl, ethyl, etc., give this reaction, as well as the ordinary salts.
2. Its methyl ether, formed by warming a salicylate with **sulphuric acid** and **wood spirit** has the odour of oil of wintergreen.

From most other solid bodies it may be separated by taking advantage of its exceptionally great solubility in ether. In the event of its presence in an organic liquid (such as milk), it or its salts may be procured in a pure condition by dialysis.

56. TANNIC, GALLIC, and PYROGALLIC ACIDS.

Tannic Acid $C_{27}H_{22}O_{17}$—is soluble in water and alcohol, and very soluble in glycerine. It is insoluble in pure dry ether, but dissolves readily in ether containing a little water.

Gallic Acid—$H_3C_7H_3O_5,H_2O$—is slightly soluble in cold water, but readily in boiling: it is also freely soluble in glycerine, and slightly in alcohol and ether.

Pyrogallic Acid—$C_6H_6O_3$ is very soluble in water, the solution rapidly absorbing oxygen from the air and becoming brown. It also dissolves in alcohol and ether.

DISTINCTION BETWEEN GALLIC, TANNIC, AND PYROGALLIC ACIDS.

BEHAVIOUR OF THE ACID WITH	GALLIC.	TANNIC.	PYROGALLIC.
Ferrous salts—$FeSO_4$.	A dark solution is formed, gradually depositing a precipitate.	The same effect as Gallic.	A blue solution.
Ferric salts—Fe_2Cl_6.	Purpish precipitate immediately formed.	Same as preceding.	A red solution.
Calcium hydrate—$Ca(OH)_2$—in the form of *Milk of Lime*.	A brownish precipitate, becoming deep brown in a few seconds.	A white precipitate slowly changing.	Instantaneous production of a purple solution becoming brown by oxidation.
Gelatine . . .	No precipitate (except in the presence of gum).	Immediate brownish precipitate.	No precipitate.

57. SEPARATION OF CHLORATES AND CHLORIDES.

Note.—The tests which follow are applicable to tests for adulterations, where, for obvious reasons, the confirmatory test for a suspected adulterant would not apply.

(Practise on mixed solutions of KCl and $KClO_3$.)

Add *excess* of argentic nitrate, filter out the argentic chloride formed, and then acidulate with sulphuric acid, and drop in a fragment of zinc, when, if a chlorate be present, a second precipitate of argentic chloride will form.

58. DETECTION OF CHLORIDES IN THE PRESENCE OF BROMIDES.

(To be practised on a mixture of KCl and KBr.)

The solution is divided into two parts, in one of which the bromide is proved by the addition of chlorine water, and shaking up with chloroform. The second portion is either (1) Evaporated to dryness, the residue placed in a tube retort with a little potassium dichromate and sulphuric acid, while into the receiver is placed a little dilute ammonium hydrate, and distillation is proceeded with, when, if a chloride be present, the liquid in the receiver will be coloured yellow; or (2) Precipitated with excess of $AgNO_3$, washed on a filter, percolated with dilute NH_4HO (1 in 20) and nitric acid added to the percolate, when a *distinctly curdy* white precipitate proves the presence of chlorides. This latter method is simple, and rarely fails if, on adding the acid, a mere cloud be disregarded.

59. DETECTION OF BROMIDES IN THE PRESENCE OF IODIDES.

(Practise on a mixture of KBr and KI.)

Add to the solution a very small quantity of starch paste and then a drop or two of chlorine water, when a blue colour will be produced, proving the iodide. Continue to add more chlorine water until this blue is entirely discharged, and then shake up with chloroform, when, if a bromide be present, the characteristic golden colour will be communicated to the chloroform.

60. DETECTION OF CHLORIDES IN THE PRESENCE OF IODIDES.

(Practise on a mixture of KCl and KI.)

Add excess of argentic nitrate, warm, pour off the supernatant liquid, wash with warm water, and shake up the precipitate in dilute solution of ammonium hydrate (1 in 3). The argentic iodide will remain insoluble, while the chloride will dissolve and may be detected in the solution, after filtration, by reprecipitation with excess of nitric acid. As argentic iodide is not *absolutely* insoluble in ammonium hydrate, a mere cloud on adding the nitric acid is to be disregarded. This test is only accurate in the insured absence of a bromide, proved as above directed (see 59).

61. SEPARATION OF AN IODIDE FROM A BROMIDE AND CHLORIDE.

(Practise on a mixture of KCl, KBr, and KI.)

1. Add to the solution a mixture of one part **cupric sulphate** and three parts **ferrous sulphate**, or mix the solution with excess of **cupric sulphate** and drop in **sulphurous acid** till precipitation ceases. The iodide will separate as cuprous iodide—Cu_2I_2—leaving the bromide and chloride in solution. Unless carefully done, this separation is not absolutely accurate, or—
2. Add to the solution **palladious nitrate** until precipitation ceases. Filter out the palladious iodide which separates, and pass **sulphuretted hydrogen** through the liquid to remove excess of palladium, and again filter. Boil to expel the excess of H_2S, and the bromide and chloride remain in solution.

62. DETECTION OF AN IODATE IN AN IODIDE.

(Practise on a solution of iodine in heated potassium hydrate—KI + KIO_3.)

When excess of tartaric acid is added to potassium iodate, iodic acid is set free; and when the same acid is added to potassium iodide, hydriodic acid is set free, and potassium hydro-tartrate formed. Thus:—

$$5KI + KIO_3 + 6H_2C_4H_4O_6 = 5HI + HIO_3 + 6KHC_4H_4O_6.$$

If these acids be thus liberated together, they immediately decompose, forming water and free iodine:—

$$5HI + HIO_3 = 3I_2 + 3H_2O.$$

If therefore starch paste and tartaric acid be added to pure potassium iodide no coloration takes place, because only hydriodic acid is liberated; but if the sample contains potassium iodate, an immediate production of free iodine ensues, which turns the starch blue.

63. DETECTION OF A SOLUBLE SULPHIDE IN PRESENCE OF A SULPHITE AND A SULPHATE.

(Practise on mixed solutions of Na_2S, Na_2SO_3, and Na_2SO_4.)

Pour the solution on a little cadmium carbonate—$CdCO_3$—filter, and treat the insoluble matter with acetic acid to remove any unacted-upon cadmium carbonate. If a sulphide has been present, a yellow residue of cadmium sulphide will remain insoluble in the acetic acid, while cadmium sulphite and sulphate will be found in the first filtrate, if these two radicals were present.

64. SEPARATION OF THIOSULPHATES FROM SULPHIDES.

(Practise on solution of commercial hyposulphite of soda, to which a drop of NH_4HS has been added.)

Having obtained a good preliminary idea by heating with H_2SO_4, add to a portion of the original solution—$ZnSO_4$—in excess, and filter.

(*a*) Precipitate white, and soluble in HCl, with smell of H_2S.
= **Sulphides.**

(*b*) A portion of filtrate heated with H_2SO_4 deposits S and smells of SO_2; and another portion added to a drop or two of ammonio-cupric sulphate instantly causes decolorisation.
= **Hyposulphites.**

65. SEPARATION OF SULPHIDES, SULPHITES, and SULPHATES.

(Practise on mixed solutions of sodium sulphite and sulphate, to which a drop of NH_4HS has been added.)

Pour the solution on an excess of cadmium carbonate, digest at a gentle heat, filter, and examine the precipitate for a sulphide as already directed (63). The filtrate, which may contain the sulphite and sulphate, is precipitated by barium chloride, the insoluble precipitate filtered out and boiled with a little hydrochloric acid, which will dissolve the barium sulphite with evolution of sulphurous anhydride—SO_2—and leave the barium sulphate insoluble.

66. SEPARATION OF SILICIC ANHYDRIDE (SILICA) FROM ALL OTHER ACIDS.

(Practise upon powdered glass.)

Fuse the substance with a large excess of $KNaCO_3$ in a platinum crucible, and when all action has ceased, cool, and boil the residue with water. The silica passes into solution with the other acid radicals, and the metals are left as oxides. Acidulate the solution with hydrochloric acid, evaporate to dryness, and heat the residue to 140° C., and maintain the heat for some time. Drench the residue with strong hydrochloric acid, then add water, and boil, when the silica will alone remain insoluble.

67. DETECTION OF A NITRITE IN THE PRESENCE OF A NITRATE.

(Practise upon potassium nitrate which has been slightly heated so as to partially decompose it.)

Add a little potassium iodide and starch paste, then introduce a small pinch of powdered metallic zinc, and lastly acidulate with acetic acid, when, if a nitrite be present, a blue colour will be produced, due to the liberation of iodine. This test is often a very necessary one when dealing with drinking water, the presence in which of nitrites, derived from the oxidation of comparatively recent organic contamination, is a dangerous indication.

68. DETECTION OF FREE NITRIC ACID IN THE PRESENCE OF A NITRATE.

Digest with excess of barium carbonate; filter, and add to the filtrate some dilute sulphuric acid, when, if the free acid is present, a precipitate of barium sulphate will be produced. This test is only good in the insured absence of any other acid capable of dissolving barium carbonate. It will also serve for detecting free hydrochloric and acetic acids in presence of their salts.

69. DETECTION OF A NITRATE IN THE PRESENCE OF AN IODIDE.

(Practise upon mixed solutions of potassium nitrate and potassium iodide.)

The fact that the addition of strong sulphuric acid liberates iodine renders the proof of a nitrate by the ordinary iron process doubtful in the presence of iodides and bromides. In this case proceed by one of the following methods:—

1. Boil with excess of potassium hydrate until any ammonium salts are decomposed, then add a fragment of zinc and again boil. Any nitrate present will be converted into ammonia, which may be recognised in the steam with moistened red litmus paper.
2. Warm with a little zinc amalgam and add a little acetic acid and starch paste, when the nitrate, being reduced to nitrite, will cause the liberation of iodine, and colour the starch paste blue.
3. Boil with stannous chloride and a large excess of hydrochloric acid, which will produce ammonium chloride from a nitrate; and by boiling the liquid with excess of potassium hydrate, the ammonia gas may be evolved. Of course the absence of ammonium salts must be first insured.

70. SEPARATION OF CHLORIDES, IODIDES, and BROMIDES FROM NITRATES.

Digest with argentic sulphate, which will precipitate the halogens as silver salts and leave the nitrate in solution.

71. SEPARATION OF CYANIDES FROM CHLORIDES.

(Practise on a mixed solution of KCN and KCl.)

Acidulate slightly with nitric acid, add *excess* of argentic nitrate, wash the precipitate thoroughly with boiling water by decantation, allow it to settle completely, pour off all the water, and boil with strong nitric acid, when the argentic cyanide is decomposed, leaving the chloride insoluble. The solution in nitric acid is diluted and hydrochloric acid added, when any dissolved silver is detected by precipitation, as chloride, thus indicating the presence of argentic cyanide in the original mixture.

72. SEPARATION OF FERRO- FROM FERRI-CYANIDES.

(Practise upon mixed solutions of potassium ferro- and ferri-cyanides.)

Acidulate with hydrochloric acid, add excess of ferric chloride, warm gently; the ferrocyanide will be precipitated. Pour off some of the brownish liquid and heat with a little zinc amalgam, when a blue precipitate will form, owing to the reduction of the ferri- to ferro-cyanide.

73. DETECTION OF CYANIDES IN THE PRESENCE OF FERRO- AND FERRI-CYANIDES.

(Practise upon mixed solutions of potassium cyanide and ferrocyanide.)

Acidulate slightly with nitric acid and add an excess of a mixture of ferrous and ferric sulphates; warm gently, and allow the precipitate to subside. Pour off a little of the supernatant liquid, add to it excess of potassium hydrate, and then acidulate with hydrochloric acid, when the production of another blue precipitate will prove the cyanide.

74. DETECTION OF A PHOSPHATE IN THE PRESENCE OF CALCIUM, BARIUM, STRONTIUM, MANGANESE, AND MAGNESIUM.

(Practise on ordinary "phosphate of lime.")

Dissolve in water by the aid of the smallest quantity of nitric acid, then add excess of ammonium acetate, which will remove the excess of nitric acid without rendering the solution alkaline. In this solution the phosphate may be proved by adding a drop or two of ferric chloride and warming, when a white precipitate of ferric phosphate—$Fe_2(PO_4)_2$—will form, insoluble in the acetic acid liberated.

75. DETECTION OF A PHOSPHATE IN THE PRESENCE OF IRON.

(Practise on ordinary "phosphate of iron.")

Dissolve in the smallest possible quantity of hydrochloric acid, add some citric acid, and then excess of ammonium hydrate. By this means an alkaline liquid is obtained, owing to the power of the organic acid to prevent the precipitation of the metal by the ammonium hydrate; and in this liquid, when cold, *magnesia mixture* (ammonio-sulphate of magnesia) causes the precipitation of white crystalline magnesium-ammonium phosphate.

76. SEPARATION OF AN ARSENIATE FROM A PHOSPHATE.

This can only be done by acidulating with hydrochloric acid, and passing a slow stream of sulphuretted hydrogen through the solution for several hours, until the whole of the arsenic is removed.

77. DETECTION OF A FORMATE IN THE PRESENCE OF FIXED ORGANIC ACIDS WHICH REDUCE SILVER SALTS.

Distil with dilute sulphuric acid at the heat of a water bath, neutralise the distillate with sodium carbonate, add a *slight* excess of acetic acid, and boil with argentic nitrate, when a dark deposit of metallic silver will form.

78. SEPARATION OF OXALATES, TARTRATES, CITRATES, AND MALATES.

(Practise upon mixed solutions of oxalic, tartaric, and citric acids.)

If the solution be acid, neutralise it with sodium hydrate; but if neutral or alkaline it is ready for use, and is treated as follows:—

A. Acidulate slightly but distinctly with acetic acid, bring the whole to the boil, and add a drop or two of calcium chloride; and if it produce a precipitate, add it till precipitation ceases. Keep the whole nearly boiling for a time, till the precipitate aggregates, and filter. This precipitate is calcium oxalate, and it should be quite insoluble in cold solution of KHO.

B. To the filtrate from *A*, mixed with some more calcium chloride, ammonium hydrate is added in slight but distinct excess, and the whole thoroughly cooled. Calcium tartrate precipitates, and when it has settled clear, the liquid is poured off and preserved for *C*. This precipitate, after washing, should be entirely soluble in cold solution of potassium hydrate, and reprecipitable by boiling.

C. The liquid is slowly boiled for some time; and if a precipitate does not form readily, a little more $CaCl_2$ and NH_4HO added, and the boiling resumed. The precipitate, when it begins to subside well, is filtered out whilst still hot. It should be (after washing) quite insoluble in cold solution of potassium hydrate, but soluble in perfectly neutral solution of cupric chloride.

D. To the filtrate add alcohol, when calcium malate will separate; but this portion of the separation is not infallible and the precipitate must be carefully examined to see that it really is malate.

79. DETECTION OF CARBOLIC ACID IN THE PRESENCE OF SALICYLIC ACID.

Boil 10 grains in half an ounce of water, cool, decant the solution, and add to it 1 minim of a saturated solution of $KHCO_3$, 1 minim of aniline, and 5 drops of solution of *chlorinated lime*, when, if carbolic acid be present, a deep blue is produced.

CHAPTER IV.

QUALITATIVE ANALYSIS, AS APPLIED TO THE DETECTION OF UNKNOWN SALTS.

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§ I. GENERAL PRELIMINARY EXAMINATION.

UNDER this head are included—

1. The observation of the physical properties of the substance submitted for analysis.
2. Its behaviour when heated, either alone or in the presence of reducing agents or fluxes.
3. Its reaction with test-papers; the colour it communicates to flame, etc.

So particular and minute may this examination be, that in the larger works on chemical analysis many pages will be found devoted to it; but for the purposes of the analysis likely to come before the ordinary chemical student, it is sufficient only to carry it the length of a few readily obtainable and unmistakable inferences. *It should also be remembered that in many cases these inferences require subsequent confirmation, and therefore a student should be taught not to jump too readily at conclusions from the preliminary investigation.*

Step 1. If the substance be a liquid, carefully mark its reaction with blue and red litmus paper, evaporate a little to dryness at a gentle heat on a clean porcelain crucible lid, observing the nature of the residue left, if any; and finally raise this residue to a red heat, carefully noting whether it is volatilised, blackened, or altered in colour any way. If a solid, heat it directly to redness on a crucible lid (or in a dry test tube), and note effect; then shake a little up with distilled water, and note its reaction with blue and red litmus paper.

From a careful study of these points, the following simple inferences may safely be drawn; *any appearance not herein referred to being neglected as not affording a really distinctive indication.*

A. **Neutral**, no odour, and leaving **no residue** whatever. Probably water.

B. **Strongly acid**, leaving **no residue**. Probably an ordinary volatile acid, such as HCl, HNO_3, $HC_2H_3O_2$, etc.

C. **Strongly acid**, leaving **a residue**, fusible by heat and also strongly acid. Probably a non-volatile mineral acid, such as H_3PO_4.

D. **Strongly acid**, leaving **a residue**, which on heating **chars**, and entirely burns away. Probably free organic acid, such as $H_2C_4H_4O_6$, $H_3C_6H_5O_7$, $HC_7H_5O_2$, etc.

Note—Oxalic and formic acids do not char.

E. **Neutral or slightly acid**, leaving **a residue**, which volatilises in fumes, but without blackening. Probably an ordinary **salt of** a volatile metal, such as NH_4, Hg, As, Sb, etc.

F. **Neutral or slightly acid**, leaving **a residue** which on **heating** blackens and volatilises in fumes. Probably an organic **salt of** NH_4, Hg, or other volatile metal.

Note.—In this case it is best at once to test the original for NH_4 or Hg by boiling with KHO and $SnCl_2$ respectively.

G. **Neutral or slightly acid**, leaving a **residue**, which on heating changes colour as follows:—

Yellow while hot, white on cooling. Probably salt of Zn.
Deep yellow while hot, yellow on cooling. Probably salt of Pb.
Yellowish-brown while hot, dirty light-yellow on cooling. Probably salt of Sn^{iv}.
Orange or red while hot, dull yellow on cooling. Probably salt of Bi.
Red while hot, reddish brown on cooling. Probably salt of Fe or Ce.
Permanent brownish-black. Certain salts of Mn.

H. **Neutral or slightly acid**, leaving a **white residue**, which blackens on heating, burns, and leaves a black or greyish mass. Probably an organic salt of a fixed metal. *In this special case, proceed as follows:—*

Moisten the residue with a little water, and touch it with reddened litmus paper. If alkaline, the original substance was an organic salt of K, Na, or Li, in which case proceed by (*a*). If not alkaline, proceed by (*b*).

(*a*) Boil the ash with the smallest possible quantity of water, filter, acidulate with HCl till effervescence ceases; dip a perfectly clean platinum wire in the solution and try the flame test. If crimson, Li. Bright yellow, Na. Violet, K.

Note.—The latter flame not being very easily seen in the daylight, it is advisable to add to the solution $PtCl_4$ and C_2H_6O. Shake well and cool. Yellow crystalline precipitate of potassium platinochloride—$PtCl_4 2KCl$. When potassium is found with a tartrate it is always necessary to test also with H_2S for antimony as the salt might be *tartar emetic.*

(*b*) The ash is covered with water and treated with $HC_2H_3O_2$. If effervescence takes place, the original substance was probably an organic salt of Ba, Sr, or Ca; and these metals may at once be tested for in the acetic acid solution.

Note.—Oxalates, although organic, do not blacken to any extent. If carefully observed, however, a slight greyish tint, followed by a distinct glow running through the mass, will be noticed at the moment of decomposition. To make certain it is well to place a little of the original powder in one tube, and the residue, after ignition, in another; cover them both with water, and add a drop of acetic acid to each. If the residue effervesce, and the original powder does not, strong presumptive evidence is obtained of the presence of an oxalate of the alkaline or earthy metals.

I. **Neutral or slightly acid**, leaving a **residue**, which takes fire and continues to burn even after removal from the flame, giving off clouds of white fumes and leaving a fixed white or pinkish residue. Probably a hypophosphite; which fact should be noted as an aid to future information as to acid radicals.

K. **Strongly alkaline**, leaving a fixed white residue, **also alkaline**. A hydrate, carbonate, bicarbonate, phosphate, arseniate, borate, sulphite, or sulphide of a fixed alkaline metal, or a hydrate or oxide of Ba, Sr, or Ca. In this case proceed as follows:—

Acidulate a portion of the original solution with HCl.

(*a*) If it effervesces without odour, and is therefore a carbonate or bicarbonate, test at once by the flame for K, Li, Na, and also another portion of the original solution with $HgCl_2$. If red, a carbonate; if not, a bicarbonate.

(*b*) Effervesces with odour of H_2S. In this case it is a sulphide; and if a deposit of S also takes place, a polysulphide. Add to a fresh portion of the original solution excess of HCl, boil till H_2S is expelled, filter, if necessary, and test the solution for all metals of fourth and fifth groups.

(*c*) Effervesces with odour of HCN. Probably an alkaline cyanide, such as KCN.

(*d*) Effervescence with odour of SO_2, an alkaline sulphite.

(*e*) It does not effervesce. In this case add to a fresh portion of the original solution, $AgNO_3$. If a brownish-black precipitate be formed, it is a soluble hydrate. A portion of the original solution should be neutralised with HCl, and then examined for all metals of fourth and fifth groups.

Note.—If $AgNO_3$ with original solution gives a yellow, a white, or a brick-red precipitate, the presence of a phosphate, borate, or arseniate of K or Na may be suspected. In the case of a complex solution in which a salt of some other metal is given dissolved in excess of an alkali, an intimation of the fact will be obtained on cautiously adding the HCl, as, at the moment of neutralisation, the dissolved substance appears as a precipitate before again dissolving in the excess of HCl. Basic plumbic acetate has an alkaline reaction.

Step 2. Dip a clean platinum wire in the solution, or, if a solid, moisten the wire with HCl, dip it in the powdered substance, and heat in the inner Bunsen or blowpipe flame. The outer flame is coloured as under :—

Violet . . .	Potassium.
Golden-yellow .	Sodium.
Yellowish-green.	Barium.
Crimson . . .	Strontium or Lithium.
Orange-red . .	Calcium.
Green . . .	Copper or Boracic acid.
Blue	Lead. Arsenic, Bismuth ; also Copper as chloride.

Step 3. Heat a little of the solid substance (or the residue left on evaporation if in solution) on charcoal before the blowpipe.

Ordinary alkaline salts fuse and sink into the charcoal ; some decrepitating (example NaCl, etc.), others deflagrating (as KNO_3, $KClO_3$, etc.), but no sufficiently characteristic indications are usually obtained, except in one of the following cases :—

A. A white luminous residue is left. Moisten it when cold with a drop or two of cobaltous nitrate, and again apply the blowpipe, observing any change of colour as follows :—

The residue becomes blue, indicating Al, Silicates, Phosphates, or Borates.
" " " green, " Zn.
" " " pink or flesh-coloured, indicating Mg.

B. A coloured residue is left. Prepare a borax bead, and heat a little of the substance in it, both in the reducing and oxidising flame, and note any colours corresponding with the following list :—

METAL.	IN OXIDISING FLAME.	IN REDUCING FLAME.
Cu *	Green (hot). Blue (cold).	Red (cold).
Co	Blue.	Blue.
Cr	Green.	Green.
Fe	Red (hot). Yellowish (cold).	Bottle-green.
Mn	Amethyst.	Colourless.
Ni	Reddish-brown (hot). Yellow (cold).	Same as oxidising flame.

C. A metallic residue is left, with or without incrustation surrounding it. Mix a little of the substance with KCN and Na_2CO_3, and expose on charcoal to the reducing flame.

(*a*) Metallic globules are produced without any surrounding incrustation of oxide. This occurs with Ag, Au, Cu, Fe, Co, and Ni, all easily recognisable.

(*b*) Metallic globules are produced with a surrounding incrustation of oxide. This occurs with Sn, Bi, Pb, and Sb ; the incrustation having the characteristic colours already described in Case I., Step 1, *G*.

Note.—Sb often forms a white and distinctly crystalline crust.

(*c*) The metal volatilises, and only leaves an incrustation of oxide. This occurs with As (odour of garlic, and white incrustation), Zn (yellow [hot], white [cold]), and Cd (reddish-brown).

§ II. DETECTION OF THE METAL PRESENT IN ANY SIMPLE SALT.

Step I. Preparation of the solution for analysis for the metal, if the substance be not already dissolved.

1. Take a minute portion of the substance and boil it with **water** in a test-tube; should it dissolve, then take a large portion and dissolve for testing.
2. Should the salt prove insoluble, take another small portion and heat with **HCl**, and add a little water and again heat. If it now dissolves, prepare a larger quantity of the solution for use in the same manner.
3. Should it resist HCl, try another small portion with **HNO_3** by heating and then adding water. If this dissolves it, make up a larger quantity of a similar solution for testing.
4. Should HNO_3 also fail, try another small portion with two parts **HCl** and one part **HNO_3**, warming and diluting as before; and if it succeeds, make up a larger amount of solution in the same manner.
5. If all acids fail, then take another portion of the substance, mix it with several times its bulk of a perfectly dry mixture of **sodium and potassium carbonates** (prepared by heating Rochelle salt in an open crucible until the residue thoroughly ceases to evolve any gases, then extracting with distilled water, filtering, evaporating to dryness, heating the residue to redness, and preserving for use in a stoppered bottle. This reagent will hereafter be shortly described as **fusion mixture**). Place the whole in a platinum crucible, and fuse at a bright-red heat; when cold, boil with water and save the solution thus obtained for acid radicals. The insoluble matter is then to be drenched with strong HCl, slightly diluted and boiled, and the solution used for testing for the metal. Any insoluble white gritty matter still remaining is put down as silica.

Step 2. Detection of the metal.

The processes to be applied vary according to the limitation of the possible substances under examination, and the following tables are to be used accordingly, using the solution obtained in Step 1. *Remember that even when we have apparently found out the metal by the table, we should always proceed to perfect confirmation by applying (to fresh portions of the solution each time) all the tests for the metal given in Chapter II.* Unless otherwise directed, all confirmations referred to in the tables are intended to be tried upon fresh portions of the original solution. For brevity the said solution is in the tables indicated by a capital **O** in thick type, and the word precipitate is contracted to ppt. In simple salts we go through the groups until we get a result, and as soon as we do we stop and go no farther with the groups, but simply confirm the result obtained by special tests.

The following brief instructions may aid the student to find readily the pages required for the full analysis of a simple salt :—

1. **Find whether soluble in H_2O or in acids, or neither.**
2. **Take the reaction**
   - acid = free acid or acid salt.
   - alkaline = complete the analysis by "K," p. 59.
   - neutral.
3. **Heat dry in a test tube**
   - does not char = inorganic salt.
   - does char = organic salt. See "H," p. 59.
4. **Find the metal by p. 64.**
5. **Find the acid radical by**
   - solubility table, p. 82.
   - If K, Na, Li, or NH_4 tables pp. 76 to 80, if inorganic.
   - ,, p. 80 if organic.
6. **Name the salt and write its chemical formula.**

FULL TABLE FOR THE DETECTION OF THE METAL IN A SOLUTION CONTAINING ONE BASE ONLY.

N.B.—In using this Table, as soon as the Metal is discovered we go no further, and all confirmations, except where specially stated, are to be applied to fresh portions of the original Solution, hereafter represented by O.

<table>
<tr><td colspan="6">1st GROUP.—Add a drop of HCl, and if it produce a precipitate, add excess.</td></tr>
<tr><td rowspan="5">PRECIPITATE
May be either
$PbCl_2$
Hg_2Cl_2
$AgCl$ } White.
CONFIRMATIONS.
Let ppt. settle, and pour off supernatant liquid; wash once by decantation with <i>cold</i> water, and then proceed as follows;—
(1.) Add some warm H_2O to ppt. and boil: if it dissolves and the solution gives a yellow with K_2CrO_4=Pb.
(2.) If ppt. insoluble in water, add to it excess of NH_4HO.
(<i>a</i>) The precipitate turns black=Hg_2 (ous).
(<i>b</i>) The precipitate dissolves and is re-precipitated by HNO_3=Ag.</td><td colspan="5">2nd GROUP.—To solution in which a drop of HCl has failed to produce a ppt. add H_2S, and if a discolouration appear, add excess and warm.</td></tr>
<tr><td rowspan="4">PRECIPITATE
May be either
HgS
PbS
Bi_2S_3
CuS
CdS
As_2S_3
Sb_2S_3
SnS
SnS_2
PtS_2
or
Au_2S_3
Let the precipitate settle, pour off as much of the supernatant liquid as possible, make the remainder alkaline by NH_4HO and add a few drops of NH_4HS and warm.
INSOLUBLE.
CdS—yellow
HgS
PbS
Bi_2S_3
CuS } Blackish
SOLUBLE.
As_2S_3
SnS_2 } Yellow.
Sb_2S_3—Orange
SnS
PtS_2
Au_2S_3 } Blksh.
CONFIRMATIONS.
(1.) <i>If ppt. yellow and insoluble in NH_4HS.</i>=Cd.
(2.) <i>If ppt. black and insoluble in NH_4HS.</i>
(<i>a</i>) Add to O, H_2SO_4: white=Pb.
(<i>b</i>) Add to O, KHO: yellow=Hg; white=Bi; and blue=Cu.
(3.) <i>If ppt. yellow and soluble in</i></td><td colspan="4">3rd GROUP (DIVISION A).—Evaporate a portion of original solution to dryness, and heat residue till any organic matter is destroyed; then dissolve in a few drops of HCl with the addition of a drop or two of HNO_3, dilute, and add NH_4Cl, and then NH_4HO in slight but distinct excess, and heat to boiling.</td></tr>
<tr><td rowspan="3">*PRECIPITATE
May be either
$Fe_2 6HO$=red-brown.
$Cr_2 6HO$=green.
Ce3OH
$Al_2 6HO$
Insol. phosph. of Fe, Cr, Al, Mn, Ba, Sr, Ca, and Mg. } White.
CONFIRMATIONS.
(I.) <i>If ppt. red.</i>
(<i>a</i>) Test O with $K_6Fe_2Cy_{12}$: dark blue=Fe.
(<i>b</i>) Test O with K_4FeCy_6: dark blue=Fe_2.
(II.) <i>If ppt. green.</i>
Evap. portion of O on a porcelain crucible lid, add some KHO and a crystal of KNO_3, again evap. to dryness and fuse: yellow residue, sol. in H_2O and precipitated yellow by Pb2Ac after acidulation by HAc=Cr.
(III.) <i>If ppt. white.</i>
(1.) Add to O, KHO; white sol. in excess and re-precipitated by boil-</td><td colspan="3">3rd GROUP (DIVISION B).—To the solution in which NH_4HO has failed to produce a precipitate, add NH_4HS, and warm for some time.</td></tr>
<tr><td rowspan="2">PRECIPITATE
May be either
MnS—flesh colrd.
ZnS—white.
CoS
NiS } black.
CONFIRMATIONS.
I. <i>If ppt. white or flesh-coloured.</i>
(1.) Test O by evaporating & fusing with KHO and KNO_3: green residue=Mn.
(2.) Test O with K_4FeCy_6: white =Zn.
II. <i>If ppt. be black,</i> boil O with KHO.
(<i>a</i>) Blueish ppt. turning pinkish on boil-</td><td colspan="2">4th GROUP.—To same solution, add $(NH_4)_2CO_3$.</td></tr>
<tr><td>PRECIPITATE
May be either
$BaCO_3$
$SrCO_3$
$CaCO_3$ } White
CONFIRMATIONS.
Let ppt. settle, pour off as much supernatant liquor as possible, and dissolve in HAc, then test successively in the same liquid.
(1.) With K_2CrO_4: yellow=Ba.
(2.) With a drop of dilute H_2SO_4 and let it stand:</td><td>5th GROUP.
——
(1). Divide into two portions; test one with Na_2HPO_4: white=Mg.
(2.) Evaporate the remainder to dryness, heat till fumes cease, dissolve residue in the smallest possible quantity of water, and try the flame test.
(<i>a</i>) Crimson flame =Li.
(<i>b</i>) Violet flame</td></tr>
</table>

	excess and not re-precipitated on boiling)=Sn (ic). (*b*) Add to O, KHO and Zn, boil and hold paper moistened with $AgNO_3$ over the tube: black stain=As. (4.) *If ppt. orange, soluble in NH_4HS,* and re-precipitated orange by HCl=Sb. (5.) *If ppt. brown or black, and soluble in NH_4HS.* (*a*) Add to O, $HgCl_2$ and boil: grey=Sn (ous.) (*b*) Add to O, $SnCl_2$: purple=Au. (*c*) Add to O, KCl and rectified spirit: yellow = Pt.	*in excess*, test O with $(NH_4)_2MoO_4$ dissolved in HNO_3 and boil. (*a*) *If no precipitate forms*, test O for Ce by evaporating and igniting and getting a red residue, which dissolves with difficulty in strong HCl, and the solution diluted and nearly neutralized gives a white with $(NH_4)_2C_2O_4$. (*b*) *If a yellow precipitate forms*, phosphoric acid is present, in which case proceed as follows:—Add to O, NH_4HO in excess, and then HAc until the solution is acid and boil. (A) *A ppt. forms*, it may be $FePO_4$, $CrPO_4$, or $AlPO_4$, filter, wash, and treat on filter with boiling dilute KHO. * *A reddish residue is left on filter*=Fe (test O for Fe and Fe_2. † *A greenish residue is left on filter*=Cr (fuse as above.) ‡ *The ppt. dissolves*=Al (confirm by boiling filtrate with NH_4Cl.) (B) *No precipitate forms.* We may have in solution the phosphates of Ba, Sr, Ca, Mn, or Mg. Test the same solution with K_2CrO_4: yellow=Ba. If no effect add a drop or two of dilute H_2SO_4, and stand for a short time: white=Sr. If not Sr add $(NH_4)_2C_2O_4$: white=Ca. If still not Ca cool and add excess of NH_4HO: white=Mg or Mn. Fuse ppt. on porcelain with KHO and KNO_3: green residue=Mn. If no green then the ppt. was Mg.	altered by boiling =Ni. (Both should be confirmed by blowpipe bead.)	$(NH_4)_2C_2O_4$: white=Ca.	=Na. Confirm K by $PtCl_4$ and rectified spirit. Test for NH_4 by boiling O with KHO and smelling.

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* As Mn may sometimes precipitate through the solution absorbing oxygen, it is always advisable to filter out a little of this precipitate and fuse it with KHO and KNO_3:—green residue=Mn.

Table for the Detection of the Metal in a Simple Salt, the Metal present being limited to the Salts commonly used and included in the Pharmacopœia.

(N.B.—*Ppt. means precipitate;* **O** *means the original solution.*)

<table>
<tr><td colspan="6">1st Group. - Add a drop of HCl, and if it produce a precipitate, add excess.</td></tr>
<tr><td rowspan="5">Precipitate.
May contain —
Pb
Hg (ous) } White.
Ag
Confirmations.
(1) Let ppt. settle; pour off liquid and add H_2O and boil. If it dissolves and gives a yellow ppt. with K_2CrO_4 — Pb.
(2) If not soluble in boiling H_2O, add NH_4HO. If now soluble — Ag. If turned black — Hg (ous).</td><td colspan="5">2nd Group.—To the solution in which HCl has failed to give a ppt. add <i>excess</i> of H_2S water and warm gently.</td></tr>
<tr><td rowspan="4">Precipitate.
(1) Notice its colour and add to it a drop of NH_4HO to neutralise, and then add 10 drops of NH_4HS and warm. Notice whether it dissolves or remains insoluble. Thus we divide the group into two divisions, as follows:—
<i>Division I.</i>
(Insoluble in NH_4HS.)
Hg
Bi
Cu } — Black.
Pb
Cd — Yellow.
If the ppt. was black, then to O add KHO.
Yellow — Hg.
Blue — Cu.
White (insoluble) — Bi.
White (soluble) — Pb.
<i>Division II.</i>
(Soluble in NH_4HS.)
Sb — Orange.
Sn(ous) — Brown.
As
Sn(ic) } — Yellow.
Test O. (1) If ppt. brown:—
With $HgCl_2$ for Sn(ous).
(2) If ppt. yellow; for As by Fleitman's test, and if not found then test specially for Sn(ic).</td><td colspan="4">3rd Group. To a <i>fresh</i> portion of O add some NH_4Cl, then NH_4HO in slight, but distinct excess, and observe effect; lastly, add a drop or two NH_4HS and again observe.</td></tr>
<tr><td rowspan="3">Precipitate.
<i>Division I.</i>
A ppt. was caused by NH_4HO, and was afterwards turned black by NH_4HS. May be Fe, provided it it is readily bleached by HCl (<i>Ni and Co not so bleached</i>).
Test O for Fe(ous) with $K_6Fe_2Cy_{12}$.
" " Fe(ic) " K_4FeCy_6.
<i>Division II.</i>
A ppt. is caused by NH_4HO not altered in colour by NH_4HS.
Green — Cr (<i>confirm by KHO</i>).
White — { Al.
Ce.
$Ca_3(PO_4)_2$.
To O add KHO.
White (soluble in excess) — Al.
White (insoluble in excess) — Ce or $Ca_3(PO_4)_2$.
Test specially for $Ca_3(PO_4)_2$ (see § V.) (Ce salts always leave a red residue on heating).
<i>Division III.</i>
Ppt. with NH_4HO instantly soluble, but NH_4HS produced a light-coloured ppt.
Flesh-coloured — Mn.
White — Zn.
Add to O chlorine water and KHO.
Brown — Mn.</td><td colspan="3">4th Group.—To the solution which has failed to give a ppt. in the 3rd group add $(NH_4)_2CO_3$.</td></tr>
<tr><td rowspan="2">Precipitate.
May contain
Ba.
Ca.
(Sr).
To O (first neutralised <i>if acid</i> by NH_4HO, and then acidulated with acetic acid) add,
(1) K_2CrO_4 yellow ppt. — Ba.
(2) $(NH_4)_2C_2O_4$ white ppt. — Ca.
Note.— If the O gives a persistent red flame, Sr is to be suspected, and its absence must then be proved before testing for Ca (see p. 25).</td><td colspan="2">5th Group. To the solution in which $(NH_4)_2CO_3$ has failed to give a ppt. add Na_2HPO_4, cool and shake.</td></tr>
<tr><td>Precipitate.
White — Mg.</td><td>6th Group.
——
(1) Test O for (NH_4) by boiling with KHO and smelling for NH_3.
(2) Test O for K with $PtCl_4$, first concentrating by evaporation and cooling: yellow ppt. — K.
(3) Apply flame test.
Yellow — Na.
Crimson — Li.</td></tr>
</table>

§ III. DETECTION OF THE METALS IN COMPLEX MIXTURES OF TWO OR MORE SALTS.

Step I. Preparation of the solution for analysis in cases where the substance for analysis is not given in solution.

Note.—By carefully applying this step and intelligently judging the results, we can often reduce a separation of two salts to the performance of two separate simple analyses, and so save much time and trouble.

1. Boil some of the powdered substance with **distilled water**, and filter off from any insoluble matter.

Evaporate a drop or two of the filtrate to dryness, at a gentle heat, on a slip of clean platinum foil, and if any residue be left, then save the balance of the filtrate for analysis as representing the portion of the original (if any) that is soluble in water.

2. If anything remains insoluble in water, then wash it on the filter with boiling water until a drop of the washings leaves no marked residue on evaporation. Rinse the insoluble portion off the paper into a tube, and add **hydrochloric acid** drop by drop (noting carefully any effervescence or odour as indicating the presence of certain acid radicals, such as carbonates, sulphides, sulphites, cyanides, etc.), and warm.

If it now all dissolves, save the fluid for analysis. If not, then separate the insoluble part, test the filtrate by evaporation of a drop or two, to see whether anything has dissolved, and if so, save the fluid for analysis as representing the metals present in the form of salts insoluble in water, but soluble in HCl.

Note.—This division of any mixture into salts soluble and insoluble in water gives the greatest assistance in the subsequent testing for the acid radicals. For example, if a metal of the 5th group be found in the portion soluble in water, then any acid radical almost may be present: while if a metal of one of the other groups be found, then generally speaking only a nitrate, sulphate, chloride, or acetate need be first searched for. If, on the other hand, the substance resists the action of water and only goes into solution with HCl, then as a rule *no metal of the 5th group is present*, and we might consider that we were probably dealing with a carbonate, oxide, phosphate, arseniate, oxalate, sulphide, sulphite, cyanide, ferro- or ferri-cyanide, or borate of a metal, not in the 5th group. Certain tartrates and citrates, chiefly of the 4th group, would also come in this category.

3. If the substance is insoluble in both water and HCl, try **nitric acid**, first alone, and then with the addition of **hydrochloric acid**.

This treatment dissolves certain metals in the free state, such as Ag, Pb, Bi, Hg, and Cu, and also acts upon Hg_2Cl_2, HgS and other insoluble sulphides, and on Fe_2O_3 and some refractory oxides. Gold and platinum dissolve only in nitro-hydrochloric acid.

Note.—When HNO_3 has been used as a solvent, the liquid should always be evaporated with HCl till all the HNO_3 has been displaced, then allowed to get quite cold and any precipitate filtered out and treated as belonging to the 1st group, while the filtrate is directly treated with H_2S.

4. If anything still remains insoluble, it must be fused with **fusion mixture** ($KNaCO_3$) at a bright red heat till action ceases, and the residue so obtained boiled with water and filtered.

The filtrate is used for the detection of acid radicals; while the insoluble matter is dissolved (after washing) in nitric acid and used for finding the metals. The usual run of articles requiring this treatment are—sand, clay, and other silicates, sulphates of Ba, Sr, Ca (latter not always), and Pb, the haloid salts of silver, SnO_2 and Sb_2O_4.

Step II. Proceed to apply the following tables to the prepared solution from Step I.

Note.—The whole of the first table for "separation into groups" must be gone through, but if no effect be obtained in Groups I. or II., a fresh portion of the prepared solution should be taken for Group III., etc., so saving the time required for evaporating to a considerable extent.

TABLE FOR THE SEPARATION OF METALS INTO GROUPS.

<table>
<tr><td colspan="6">Add a drop of HCl and if it produce a precipitate, add excess (<i>Note</i> 1).</td></tr>
<tr><td rowspan="5">the ppt. may contain
$PbCl_2$
Hg_2Cl_2
$AgCl$,
and is collected on a filter and examined by Table A.
GROUP I.</td><td colspan="5">To the filtrate add H_2S water, and if it produce a discoloration, warm to blood-heat and pass H_2S in excess.</td></tr>
<tr><td rowspan="4">The precipitate is to be carefully washed with boiling H_2O till quite free from HCl (<i>Note</i> 2). It is then to be washed into a test-tube about half-full of H_2O, and from 10 to 20 drops of NH_4HS having been added, the whole is warmed for a time and filtered (<i>Note</i> 5).
(<i>a</i>) Insoluble portion, including possibly
HgS
PbS
Bi_2S_3
CuS
CdS,
is examined by Table B.
(<i>b</i>) Soluble portion, containing possibly
As_2S_3
Sb_2S_3
SnS
SnS_2
Au_2S_3
PtS_2,
is examined by Table C.
GROUP II.</td><td colspan="4">Evaporate filtrate to dryness in a platinum capsule, and heat till any organic matter present is decomposed. Moisten the residue with strong HCl, and then add H_2O and boil (any insoluble (<i>Note</i> 3) if white = SiO_2). Take a little of the solution, add HNO_3 and $(NH_4)_2MoO_4$ and boil. If Phosphates be present, a yellow precipitate will be produced (<i>Note</i> 4). Take now the rest of the solution, warm it with a drop or two of HNO_3 and then add NH_4Cl and NH_4HO, the latter in slight but distinct excess; boil and filter (<i>a</i>). Add to the filtrate NH_4HS in excess, boil and filter (<i>b</i>).</td></tr>
<tr><td rowspan="3">(<i>a</i>) NH_4HO
Precipitate may (in absence of PO_4) contain
$Fe_2 6HO$
$Cr_2 6HO$
$Al_2 6HO$
Ce_3OH
Wash with boiling H_2O and examine by Table D.
(In presence of PO_4)
It may contain
$FePO_4$
$AlPO_4$
$CrPO_4$
$CePO_4$
Ba_32PO_4
Sr_32PO_4
Ca_32PO_4
Mn_32PO_4
Mg_32PO_4
Wash with boiling water and examine by Table E.
Division (a). GROUP III.</td><td rowspan="3">(<i>b</i>) NH_4HS
Precipitate may contain
MnS
ZnS
NiS
CoS
Wash with H_2O containing NH_4HS and examined by Table F.
Division (b).</td><td colspan="2">Add to filtrate $(NH_4)_2CO_3$ and boil.</td></tr>
<tr><td>Precipitate may contain
$BaCO_3$
$SrCO_3$
$CaCO_3$
examined by Table G.
GROUP IV.</td><td>Filtrate may contain
Mg
Li
K
Na
examined by Table II.
GROUP V.</td></tr>
<tr><td colspan="2">NOTES.
(1) Too much excess HCl prevents the rapid precipitation of Cd by H_2S.
(2) Known by testing washings with $AgNO_3$ and continuing to wash and test till no precipitate is produced.
(3) Cerium leaves a very dark red residue only soluble in strong acid.
(4) A little patience here, as in dilute solutions the precipitate does not form instantly.
(5) When Cu is suspected from the Preliminary Examination, take care not to use yellow NH_4HS as it always dissolves some CuS.</td></tr>
</table>

TABLE A.

SEPARATION OF METALS OF GROUP I.

<table>
<tr><td colspan="3">After washing the precipitate once with cold water; put the funnel over a fresh tube and pour on some boiling water.</td></tr>
<tr><td rowspan="2">The filtrate may contain
$PbCl_2$
Test while still hot with K_2CrO_4
Yellow Precipitate = Pb.</td><td colspan="2">Any precipitate remaining on the filter is washed with boiling water till all trace of Pb is removed, and then percolated with dilute NH_4HO (1 to 3).</td></tr>
<tr><td>Any black precipitate which remains on the filter is NH_2Hg_2Cl, and proves the presence of Hg.</td><td>The filtrate is diluted ~~with an equal bulk of water, and then cautiously~~ acidulated with HNO_3 ~~(to re-precipitate AgCl previously dissolved by the NH_4HO)~~.
White precipitate = Ag.</td></tr>
<tr><td colspan="3">NOTE.—Instead of filtering, the whole of this analysis may be done by decantation, as the precipitates are heavy and settle rapidly.</td></tr>
</table>

TABLE B.

SEPARATION OF METALS OF GROUP II., DIVISION (a).

Wash precipitate with boiling water, and then transfer it to a small porcelain dish, add a few drops of HNO_3, and warm till red fumes cease, and repeat this heating with HNO_3 till an additional drop fails to cause any more red fumes. Now wash the contents of the basin into a tube with a little water (1), add H_2SO_4 till no more precipitate forms, then cool and add an equal bulk of spirit of wine (methylated).

<table>
<tr>
<td rowspan="2">Any Precipitate may contain HgS (2), and $PbSO_4$. Percolate with a strong solution of $NH_4C_2H_3O_2$, and test filtrate with K_2CrO_4. Yellow = Pb.
Any black residue now remaining in the filter will be HgS, and is to be confirmed by dissolving in HCl by the aid of a crystal of $KClO_3$, and (after boiling free from Cl) adding $SnCl_2$, and boiling. Grey precipitate = Hg.</td>
<td colspan="2">To the Filtrate, which may still contain Bi, Cu, and Cd, add NH_4HO in excess.</td>
</tr>
<tr>
<td>Any Precipitate will be Bi3HO, and is to be confirmed by dissolving in the least possible quantity of HCl by the aid of heat, and pouring into H_2O.
White = Bi.</td>
<td>The Filtrate, if blue in colour, contains Cu for certain, and possibly also Cd. If not blue, no Cu is present, and Cd is to be directly tested for by adding NH_4HS. Yellow ppt. = Cd. If Cu be present, then add KCy until the blue colour is discharged, and pass H_2S, when any Cd will be precipitated as yellow CdS.</td>
</tr>
</table>

Note 1.—Too much water added might precipitate any Bi, as Oxy-Nitrate.

2.—If any Cl have been left in the original group precipitate (through inefficient washing) the HgS will dissolve and be lost.

TABLE C.

SEPARATION OF METALS OF GROUP II., DIVISION (b).

First Method, in Absence of Gold and Platinum.

Acidulate with HCl to cause the reprecipitation of the sulphides. If a decided yellow, orange, or black precipitate separates, then proceed to filter out; but if only a cloud of precipitated sulphur forms (not separating readily, and nearly white in colour), no metals of this division are present. After washing the sulphides, suspend them in a cold solution of the B.P. ammonium carbonate, shake up for a few minutes, and filter.

The **filtrate** may contain $(NH_4)_3AsS_4$. Add HCl in excess, and if present As will be reprecipitated as yellow As_2S_3. Filter out and confirm by drying and heating with KCy and Na_2CO_3 in a small tube, thus getting a mirror of metallic arsenic, or, if preferred, by Fleitman's test.

Any **orange** or **yellow precipitate** still remaining may be sulphides of Sb or $Sn^{(ic)}$. Dissolve in strong boiling HCl, dilute a little, and put into a platinum dish with a rod of zinc so held that it dips in the fluid and touches the platinum outside the liquid. Electrolysis will set in and cause the Sb to deposit as a black stain closely adhering to the platinum, while Sn will deposit as loose metallic granules. Boil with HCl (after washing) and the Sn will dissolve, forming $SnCl_2$ and giving a precipitate with $HgCl_2$; while the Sb will remain undissolved, and may be confirmed by oxidizing with a drop of HNO_3, then dissolving in solution of $H_2C_4H_4O_6$ and getting the characteristic precipitate with H_2S.

Second Method in Presence of Gold and Platinum.

When the precipitate from the NH_4HS by dilute HCl is dark in colour, either $Sn^{(ous)}$ Au or Pt must be present. In this case the separation had better be conducted as follows. Boil the mixed sulphides at once with strong HCl as long as H_2S is given off; dilute slightly, and filter.

Filtrate may contain $SbCl_3$ and $SnCl_2$, which are separated by electrolytic process above described.

Precipitate may contain As_2S_3, Au_2S_3, and PtS_2. If it be yellow, simply confirm the As by fusion in a tube as above; but if it be blackish, then Au or Pt are certainly present. In this case digest the precipitate with solution of ammonium carbonate as above.

Filtrate may contain $(NH_4)_3AsS_4$. Reprecipitate with HCl, and prove by fusion as above.

Precipitate may be Au_2S_3 and PtS_2. Dissolve in aqua regia; dilute, and test a portion for Au with $SnCl_2$ (Purple = Au), and another for Pt by KCl and S.V.R. Yellow = Pt.

TABLE D.

SEPARATION OF METALS OF GROUP III., DIVISION (a).

(*Note* 1.) Wash and transfer to a platinum or silver dish, and fuse with $KNaCO_3$ and KNO_3. Boil the residue in water and filter.

<table>
<tr>
<td rowspan="2">Insoluble portion may contain Fe and Ce. (<i>Note</i> 2.) Moisten with strong HCl, and then add H_2O and boil. Test a portion of the solution for Fe by K_4FeCy_6. Blue ppt. = Fe. To remainder add citric acid, and then excess of NH_4HO, and finally $(NH_4)_2C_2O_4$. White ppt. = Ce</td>
<td colspan="2">The solution (<i>which if yellow contains</i> Cr) is mixed with Na_2HPO_4 acidulated with $HC_2H_3O_2$ and boiled.</td>
</tr>
<tr>
<td>Precipitate is $AlPO_4$.
Gelatinous white = Al.</td>
<td>Filtrate treated with $AgNO_3$ gives a red, or with $BaCl_2$ a yellow if Cr be present (<i>Note</i> 3).</td>
</tr>
</table>

NOTES.

1. If this group precipitate be deep reddish-brown, nothing is probably present but Fe. If it be at all greenish, Cr is present. If it be white or pale red, take a little on a watch-glass, and touch it with an excess of KHO and observe effect.

   Originally white and soluble, only Al.
   „ „ insoluble „ Ce.
   „ pale red, and becoming deep red, and partly dissolving, Fe and Al both present (probably).
   „ „ „ not darkened by KHO, but darkened by NaClO, Fe and Ce both present.

2. If Ce be present, the red residue is with great difficulty soluble, even in strong HCl.
3. Sometimes the NH_4HO brings down Mn along with the Fe in this group; and both the residue and solution being then bright green, the yellow of the Cr is of course masked. In this case boil the filtrate with HCl and alcohol when the green of the manganate will be removed, while the chromate will be reduced to Cr_2Cl_6 and turned greenish. If therefore the originally green solution be entirely decoloured by HCl and alcohol nothing but Mn was present; but if a green tint remain, then Cr was also present. This is of rare occurrence, but must always be kept in view when the original fusion gives a green residue.

TABLE K.

SEPARATION OF METALS OF GROUP III. (DIVISION a) IN PRESENCE OF PHOSPHORIC ACID.

(*Note* 1.) Dissolve precipitate in dilute HCl, add excess of Na_2HPO_4 and then excess of $NH_4C_2H_3O_2$ and boil.

<table>
<tr>
<td colspan="2">Precipitate may be
(<i>Note</i> 2) $FePO_4$, $AlPO_4$, $CePO_4$ wash with boiling H_2O and percolate with some boiling dilute KHO.</td>
<td colspan="4">Filtrate, if green in colour, contains Cr. (but if perfectly colourless, that metal may be noted as absent). Add K_2CrO_4 and warm.</td>
</tr>
<tr>
<td rowspan="3">Residue may contain
Fe and Ce
Dissolve in HCl and test a portion for Fe by K_4FeCy_6.
Blue = Fe.
To the remainder add citric acid and then NH_4HO in excess. An immediate white or a white after adding $(NH_4)_2C_2O_4$ = Ce.</td>
<td rowspan="3">Filtrate may contain
$AlPO_4$
supersaturate with $HC_2H_3O_2$.
White gelatinous = Al.</td>
<td rowspan="3">Precipitate
$BaCrO_4$.
Yellow = Ba.</td>
<td colspan="3">Filtrate must be tested for Sr by flame test (If present, <i>Note</i> 3), if absent, proceed as follows. Add $(NH_4)_2C_2O_4$.</td>
</tr>
<tr>
<td rowspan="2">Precipitate
is CaC_2O_4.
White = Ca.</td>
<td colspan="2">Filtrate is mixed with a little $H_3C_6H_5O_7$ cooled and excess of NH_4HO added (<i>Note</i> 4).</td>
</tr>
<tr>
<td>Precipitate may contain
Mn_22PO_4 or Mg_22PO_4
(See <i>Note</i> 5).
Separation, if necessary, by dissolving in dilute HCl, adding excess of $NH_4C_2H_3O_2$, boiling, and dropping in Fe_2Cl_6 till a reddish tint is produced. Filter out the $FePO_4$ thus produced, and to the filtrate add NH_4Cl, NH_4HO, and NH_4HS, to remove Mn and Fe. Again filter, concentrate to a small bulk, and test when quite cold for Mg by NH_4HO and Na_2HPO_4.</td>
<td>Filtrate
may contain
Cr only,
prove by fusion in original.</td>
</tr>
</table>

NOTES.

1. This precipitate, if free from Ce, Cr, and Mn, is much more simply worked. Therefore take a little before dissolving and put it on a porcelain crucible-lid with a few drops of strong KHO and a crystal of KNO_3, evaporate to dryness and fuse. If no bright yellow or green residue be formed Cr and Mn are respectively absent. Take another portion of the group precipitate on a white porcelain lid, and add some solution of chlorinated soda or lime; if it does not turn yellow, then Ce is absent (if Mn be present this last test will turn the precipitate brown) so that it is only when it does not change colour at all that the positive absence of Ce can be insured.
2. Here $CrPO_4$ should be found, as it is theoretically insoluble in acetic acid; but in practice it is, when freshly precipitated, nearly entirely soluble, and passes on as shown in the Table. If its presence is suspected, a little of the precipitate may be fused as above.
3. If Sr be present (known by its crimson flame, and distinguished from the mere orange-red of Ca) it must be removed by adding a little very dilute H_2SO_4, letting stand for twenty minutes in a warm place, and then filtering out the $SrSO_4$ formed. In this case excess of ammonium acetate must be added before proceeding to test for Ca.
4. If no Cr is present the citric acid need not be used, as it is only added to prevent the precipitation of $CrPO_4$ by the NH_4HO.
5. If no Mn was found by the preliminary fusion (*Note* 1) this precipitate is all Mg; but if Mn be present it must be first removed before Mg can be definitely proved.

TABLE F.

SEPARATION OF METALS OF GROUP III., DIVISION (b).

CASE I.—If the group precipitate be white or flesh-coloured, nothing is present but MnS and ZnS; and it then only remains to dissolve in dilute HCl, add NaHO in excess, boil, and filter.

The **filtrate** may contain Zn dissolved in excess of NaHO; add excess of $HC_2H_3O_2$ and then K_4FeCy_6. White ppt. = Zn	Any **precipitate** may be Mn_2HO, which must be confirmed by fusion on platinum foil with $KNaCO_3$ and KNO_3. Green residue = Mn. (*Note.*) The supposed precipitate of Mn must be confirmed, because any trace of Fe escaping precipitation in its own group might appear here as Mn.

CASE II.—If the group precipitate be dark in colour, then Co and Ni may also be present. In this case a black residue of NiS and CoS will remain insoluble in the diluted HCl. Any such residue must be filtered out and dissolved in strong boiling HCl, or Aqua Regia, if necessary; then add excess of KCy, and boil in the fume chamber, adding more HCl if necessary, until all further smell of HCy ceases to be developed. Then add KHO in excess.

Any **precipitate** contains Ni; confirm by drying and heating in borax bead.	The **filtrate** may contain Co; confirm by evaporating to dryness, and heating residue in borax bead.

TABLE Q.

SEPARATION OF METALS OF GROUP IV.

Dissolve the precipitate in $HC_2H_3O_2$ and add K_2CrO_4 in excess.

<table>
<tr>
<td rowspan="2">Any precipitate is
$BaCrO_4$. Yellow = Ba.</td>
<td colspan="2">Take a <i>small portion</i> of the filtrate and add some saturated solution of calcium sulphate, warming gently. If no precipitate should form, Ca only is present, and may be confirmed at once by adding $(NH_4)_2C_2O_4$ to the <i>remainder of the filtrate.</i> But if a precipitate be produced Sr is present, and must be separated by adding a few drops of very dilute H_2SO to the said <i>remainder</i>, and letting the whole stand in a warm place for fifteen or twenty minutes.</td>
</tr>
<tr>
<td>Any precipitate is $SrSO_4$; confirmed by being perfectly insoluble after digestion for some time at a gentle heat with a strong solution of $(NH_4)_2SO_4$ and a little NH_4HO (to remove any $CaSO_4$ accidentally precipitated). White residue giving crimson flame = Sr.</td>
<td>The filtrate may contain Ca, confirmed by adding NH_4HO and $(NH_4)_2C_2O_4$. White = Ca.
(<i>Note.</i>) To ensure that Sr is fully separated, see that a portion of this filtrate gives no precipitate by warming with a saturated solution of $Ca\ SO_4$.</td>
</tr>
</table>

TABLE H.

SEPARATION OF METALS OF GROUP V.

Divide the solution into ⅓ and ⅔. Take the ⅓ portion, and concentrate by evaporation if very dilute, cool perfectly, and add excess of NH_4HO and Na_2HPO_4. White = Mg. Evaporate the filtrate to dryness on the water bath, and take up with *boiling water*, when any white insoluble residue is Li, provided it gives a crimson flame on a platinum wire previously dipped in HCl.

Take the remaining ⅔ and evaporate to dryness, and heat till all fumes of ammonium salts cease to be evolved. Take up the residue with the smallest quantity of boiling water (pouring off from and disregarding any insoluble matter). Then acidulate with HCl, dip in a wire and test flame, looking first at it with the naked eye, and then through a piece of blue glass (to cut off the sodium yellow).

Red	Li (disregard if already found in the ⅓ portion).
Yellow	Na.
Violet	K.

Confirm K by adding $PtCl_4$ to the rest of the acidulated solution, and getting when cold a yellow precipitate of $PtCl_4 2KCl$.

Test for NH_4 by boiling some of the original solution with KHO, and getting off NH_3.

§ IV. DETECTION OF THE ACID RADICALS.

Division A.—Preliminary Examination.

IMPORTANT NOTE.—We must always decide what metals or bases are present before we proceed to test for acid radicals. We must then note which bases are present as *soluble* and which as *insoluble* salts (in H_2O). Lastly, we must consider what acids might be present in each case, and only test for such possible acids, because *nothing leads to so many errors as testing for acids which could not possibly exist.* We must also carefully note the information received in the former preliminary examination, especially as regards the presence of organic matter, and remember that, if the original substance does not char on heating *we must never enter into the testing for organic acids*, because none can possibly be present except oxalate, which is provided for in the inorganic portion of the course with this very object, together with a few others included for convenience. We must also remember to note what happens when we dissolve the original substance in HCl, provided such a step is necessary, and if any effervescence occurs we must be sure to smell the gas given off, because we may then at once detect the following:—

*Carbonate . .	effervescence without odour, and the evolved gas poured into lime-water renders it milky.
*Sulphide . .	odour of H_2S (with deposit of S polysulphide).
*Sulphite . .	„ SO_2 („ „ hyposulphite).
*Cyanide . .	„ HCN.
Peroxide . .	„ chlorine.

Fe, Zn, or Sn (as metals)—Hydrogen evolved; without odour.

We must also remember that organic bodies, such as alkaloids or sugar, other than organic salts, might be contained in a mixture which would cause charring on heating, and so lead us to test for what was not there. It will be useful at this point to see how we can guard against two of the more commonly occurring of such cases.

(1) *Sugar.* This will cause the soluble portion to be syrupy, and when warmed with *dilute* H_2SO_4 it will rapidly darken, whereas organic salts, as a rule, require fairly strong H_2SO_4 to char them. The solution will have a sweet taste, and after boiling with a drop or two of very dilute H_2SO_4 it will reduce Fehling's solution.

(2) *Alkaloids* (nitrogenous organic bases). These will cause an odour like burning hair on heating to redness. The soluble portion of the mixture carefully treated with very dilute NH_4HO will usually give a cloud (which may or may not dissolve in excess), and then the same liquid shaken up with chloroform, and the chloroform evaporated at a *gentle* heat, will leave the alkaloid as a residue. If no residue be thus obtained, then no alkaloid can be present except morphia, and this latter would never be put in a mixture unless specially intended for toxicological inves-

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[*] In soluble salts these effects will come on adding HCl in Group I.

tigation, because its detection requires altogether special work, which will be afterwards detailed.

Having well considered all this, we now proceed to the actual work, carefully remembering that all the indications are merely preliminary, and that we are *not to take notice unless we really get a distinct result.* If we really do get one, then it may save us going so far through our actual acid course, but if we are not certain, then it is no use attempting to persuade ourselves and wasting time, but we should just note the probability and then at once pass on to confirm by the actual course hereafter detailed.

No attempt is made to describe odours, because the student should simply put himself through a course of training for this preliminary examination on known salts, and learn to recognise all the odours, etc. This is a most important study, and should be carefully stuck to, until the nose and eyes have been quite trained to recognise the individual effects to be expected from each acid.

Step I. Put a portion of the original solution in a tube, or if it be a solid cover it with some water, *just acidulate* with *dilute* **H_2SO_4**, and look for **any** effervescence or odour, then boil and smell. The following radicals may be thus recognised :—

Effervescence without odour . . .	Carbonate.
Effervescence with characteristic odours .	Sulphide. Sulphite. Cyanide. Hypochlorite.
Red fumes	Nitrite.

Step II. Add another drop of **H_2SO_4**, and again **warm.**

Odour of vinegar	Acetate.
„ „ SO_2 with deposit of S . .	Hyposulphite.
„ „ HCN „ „ „ . .	Sulphocyanate.
„ „ HCN „ crystalline deposit, often bluish	*Ferro-* or *Ferri*-cyanide.
„ „ Valerian or sharp odour	Valerianate, Benzoate, Succinate.
„ „ Carbolic acid . . .	Carbolate.

Note.—The effects of Step II. will often come perfectly in Step I. and then Step II. may be considered as part of Step I.

Step III. Put a little of the original solid (or the residue left on evaporation if the original was a liquid) into a dry tube, cover it with **strong H_2SO_4**, and warm, but not sufficiently to cause the H_2SO_4 itself to fume. *(See note, important to prevent accidents.)*

Thus we get :—

White fumes (characteristic of)	Chloride. Nitrate. Fluoride. Benzoate. Succinate. Sulpho-carbolate.	Change of colour and coloured fumes (characteristic of)	Iodide. Iodate. Bromide. Bromate. Chlorate.

Effervescence on warming only, which persists after withdrawing from flame, but with *no* darkening in colour and no odour.	*Formates*—give off CO only, and consequently the gas does not affect lime-water. *Oxalates*—give both CO and CO_2, and the gas therefore renders lime-water milky.
Effervescence on warming, but the liquid darkens in colour to a greater or less extent.	*Tartrates*—rapid charring and smell of burnt sugar. *Lactates*—not so dark, and peculiar odour. *Citrates*—slow darkening and peculiar sharp odour. *Oleates*—char and give odour of acrolein.
Darkening in colour without any very marked effervescence.	Meconate. Tannate. Gallate. Pyrogallate. Salicylate (*very* slow darkening).

No fumes—gelatinous deposit (or flaky)—Silicate.

„ „ —scaly crystals with pearly lustre—Borate (best seen on cooling).

No change takes place at all with—Sulphate, phosphate, and arseniate.

Chromates turn orange and then green—Bichromates turn green straight off.

NOTE, IMPORTANT.—*On adding strong sulphuric acid to any solid, one drop only should be first carefully applied, because chlorates, iodates, etc., are apt to explode on the first touch of the acid.*

If we get a decided indication of the presence of any acid radical as above, we may at once apply confirmatory tests for the radical found to our original substance, and so save going through the course, especially if the substance be soluble in water; but if insoluble, a solution must always be specially prepared for acid testing.

Division B.—Preparation of a Solution for Testing for Acid Radical.

The success of the course for the detection of acids depends in the highest degree upon the care with which the solution is first prepared. It may be taken as a general rule that no testing for acids is reliable unless they are present in the form of salts of alkaline metals. It is therefore necessary to transform our acids into such salts; and, to do this successfully, the following rules must be closely adhered to:—

I. If the original is soluble in water, and *absolutely neutral* to test-paper, you may venture as a rule to use it as it is, and this will also apply, if it be *alkaline*, to test-paper.

II. If the original be soluble in water, but in the least acid, we must drop in NaHO till it is rendered just *alkaline*, boil, and, if any precipitate should form, filter and use the filtrate for the acid course.

III. The portion insoluble in water (or the whole of the original if all insoluble) must be boiled with a little NaHO, then diluted, filtered, and the filtrate only used for the acid course.

Note.—If Al, Zn, Sb, Sn, Cr, Pb, or any metal whose hydrate is soluble in excess of NaHO has been found, then we must use a solution of Na_2CO_3 instead of NaHO in both Cases II. and III.

We must also take care to prepare plenty of our solution, because if the full acid course has to be gone through, we shall require possibly to employ eight to ten different portions before we have finished.

This course now about to be explained is so devised that by working upon the prepared solution, in the presence successively of HCl, HNO_3, $HC_2H_3O_2$, H_2SO_4 and absolute neutrality, we can insure the precipitation in each stage of certain given acid radicals only by reagents, which, if used without such precautions, would precipitate many more than they do when so employed.

Division C.—Course for the Detection of Inorganic Acids together with a few Organic included for certain reasons.

Step I. Acidulate a portion of the prepared solution with **HCl**, and then to successive portions thereof apply the following tests:—

REAGENT.	EFFECT.	ACID PRESENT.
(*a*) $BaCl_2$	White ppt. insoluble in boiling HNO_3 . .	Sulphate.
(*b*) Fe_2Cl_6	Dark blue ppt.	Ferrocyanide.
	Blood red colour discharged by $HgCl_2$ . .	Sulphocyanate.
	Blood red colour not discharged by $HgCl_2$ . .	Meconate.
(*c*) $FeSO_4$	Dark blue	Ferricyanide.
(*d*) Turmeric paper .	Dip in and dry over the gas when the paper turns pink, changed to green by KHO. .	Borate.

Step II. Acidulate a portion of the prepared solution with **HNO_3**, add *excess* of **$AgNO_3$**, warm and shake, *disregarding any precipitate that is not white or yellow and distinctly curdy.* Thus we get the following:—

(*a*) **Cyanide**– Curdy white; soluble in very dilute NH_4HO, and also in boiling HNO_3.

(*b*) **Chloride**– Curdy white; soluble in very dilute NH_4HO, but insoluble in boiling HNO_3.

(*c*) **Bromide**– Curdy dirty white; slowly soluble in fairly strong NH_4HO, but not in very dilute; insoluble in HNO_3.

(*d*) **Iodide** Curdy pale yellow; insoluble even in strong NH_4HO and also in HNO_3.

Note. Many other acids, such as ferrocyanide, oxalate, chromate, etc., are apt to come down with $AgNO_3$ in presence even of HNO_3, but the precipitates are (if white) *not curdy*, or they are coloured red and so will be disregarded; and we therefore deal only with the four acids mentioned giving curdy precipitates.

To distinguish between these four acids we—

(1) **Filter** out the precipitate with $AgNO_3$, wash it, and then percolate it **several** times with very dilute NH_4HO (1 in 20), when AgCl and AgCN will dissolve, and can be reprecipitated from the filtrate by HNO_3, while any AgBr or AgI will be left on the filter.

Note.—It is very important to have the dilute NH_4HO exactly 1 in 20, because, if stronger, then AgBr will also dissolve, and in any case a *mere cloud on adding the HNO_3 is to be disregarded*, because if AgCl or AgCN be really present, they will reprecipitate in distinct curds, on adding HNO_3, warming and shaking.

(2) If by (1) evidence of the presence of Cl or CN be obtained, then test a portion of the original prepared solution for CN by Scheele's test, and if not present then the precipitate was all due to Cl. If CN be found, then another precipitate must be obtained by excess of $AgNO_3$, filtered, washed, drained, and transferred to a tube with strong HNO_3 and boiled, when any AgCl will remain insoluble.

Note.—As HCN is so easily smelt in the preliminary examination, we should always know before we begin the group whether it is there, and then if it be present the boiling with HNO_3 will be required, but if not, then we put it down at once as chloride if the NH_4HO dissolves anything.

(3) If, after treating with NH_4HO (1 in 20), any residue be left on the filter, leading to the idea that AgBr or AgI may be present, we proceed as follows: To a *small* portion of our prepared solution a drop of mucilage of starch is added, and then one or two drops of chlorine water. If **iodide** be present we shall get a blue. Now we go on adding fresh chlorine water till all the blue has been bleached, and if the whole is now perfectly white only iodide is present; but if it remain at all yellow, then we add some chloroform and shake up, when an orange colour in the chloroform will indicate **bromide**. This depends on the fact that free iodine combines with chlorine more readily than with bromine.

Step III. Acidulate a portion of the prepared solution with **acetic acid**, bring it to the boil, and then test successive portions while boiling as follows:—

REAGENT.	EFFECT.	ACID PRESENT.
(*a*) $CaCl_2$	White ppt. soluble in HCl .	Oxalate.
(*b*) Fe_2Cl_6 (*not* in excess) .	White ppt.	Phosphate or Arseniate.
(*c*) $Pb(C_2H_3O_2)_2$ . .	Yellow ppt.	Chromate.

To distinguish between phosphate and arseniate *exactly* neutralise a portion of the prepared solution with dilute $\mathbf{HNO_3}$ and add $\mathbf{AgNO_3}$.

Yellow precipitate soluble in NH_4HO = Phosphate
Red „ „ „ = Arseniate

Step IV. *Just acidulate* a portion of the prepared solution with **dilute H_2SO_4**, then add a strong and fresh solution of **$FeSO_4$**, and run some strong **H_2SO_4** down the side of the tube so that it collects at the bottom. A dark ring where the liquids meet proves **Nitrate.**

Note.—If *iodide* has been previously found, this test fails to be conclusive, and in such case we must take advantage of the power of nascent hydrogen to reduce nitrates to ammonia. If no salt of NH_4 has been found in metal testing, we add to some of the prepared solution a fragment of zinc and sufficient HCl to cause a brisk effervescence. After ten minutes we add excess of KHO and boil, when an odour of NH_3 proves **Nitrate.** If NH_4 salts be present we add a little KHO to the prepared solution, evaporate to dryness, heat the residue till no more fumes are evolved, and then dissolve in water and apply the zinc, etc., as above described.

Extra Step. Iodates being very difficult to detect in the preliminary, it is well to test for them specially (if they can possibly be present) by adding to the prepared solution **KI** and **starch paste**, and acidulating with **tartaric acid**. This is not reliable in presence of nitrites.

Division D.—Course for the Detection of Organic Acids.

(Only to be entered upon in the event of the original substance being proved to contain organic matter by charring on heating in the preliminary examination.)

The solution to be used is that prepared for acid testing, as already described.

Step I. Place a minute fragment of litmus paper in a little of the prepared solution and add **acetic acid** drop by drop with agitation until the paper *just* turns red, then take out the paper and add **$AgNO_3$** in excess, lastly add a drop or two of very dilute **NH_4HO** till the precipitate *just commences* to redissolve. Now warm the tube in the Bunsen flame, when a reduction to metallic silver, forming a mirror on the tube = **Tartrate.**

Note.—The tube used must first be rendered chemically clean by boiling in it successively some dilute HNO_3 and then some dilute NaHO, and rinsing with distilled water. **Formates** produce the same effect, but do not char on heating.

Step II. Place a minute fragment of test-paper into a portion of the prepared solution, and drop in dilute HCl till it *just* turns red, then dilute NH_4HO till it *just* turns blue again, cool thoroughly, add some **$CaCl_2$** and shake well. If a precipitate forms (oxalate, tartrate, etc.), add excess of **$CaCl_2$**, shake, and let it stand in cold water for ten minutes and filter. Now add to the filtrate a little more **NH_4HO** and boil *gently* for some time, when a white precipitate = **Citrate.**

Note.—If $CaCl_2$ gives nothing in the cold, of course we simply warm for the citrate straight off. As oxalate, tartrate, etc., have all been previously tested for, we shall know, before commencing to test for a citrate, whether we need to separate them in the cold or simply to add the NH_4HO and $CaCl_2$ and boil straight away.

The addition of rectified spirit to the solution in which boiling has failed to [illegible] citrate will bring down a *Malate* on cooling, but unless specially suspected this reaction is not a very certain one.

Step III. Place a fragment of test-paper into a portion of the prepared solution, and if alkaline, make it *exactly neutral* by carefully dropping in dilute HCl. Then apply the following tests to portions of the neutralised liquid:—

(*a*) **Prepare** some neutral ferric chloride, by adding very dilute NH_4HO to a solution of Fe_2Cl_6 until a permanent cloud just forms, and filtering.

Now add some of this reagent, and observe effect as follows:—

(1) **Red colour**	Acetate Sulphocyanate Meconate Pyrogallate	(2) Purple colour	Carbolate Sulphocarbolate Salicylate
(3) **Blue-black**	Gallate Tannate	(4) Pinkish precipitate	Benzoate Succinate

Notes.

(1) **Acetate**, red, is instantly discharged by a drop of HCl; pyrogallate is turned black by excess of KHO and exposure to air. Sulphocyanate and meconate have been already proved in the inorganic acid course, but distinguished by action of $HgCl_2$ if desired.

(2) Acidulate a portion of prepared solution with HCl and shake up with ether. Remove the ether by a pipette and evaporate it on a watch-glass at a *very* gentle heat. **Carbolic acid** is left, an oily liquid readily recognised, while **salicylic acid** is left in characteristic crystals, as giving a beautiful violet with Fe_2Cl_6. (Also see page 57 for another separation.) **Sulphocarbolic acid** gives no immediate precipitate with $BaCl_2$, but on evaporating with a little Na_2CO_3 and KNO_3, and fusing, then the residue dissolved in H_2O shows a sulphate with $BaCl_2$.

(3) With excess of KHO a solution of **gallic acid** rapidly becomes dark on exposure to the air, while **tannic acid** gives a flocculent liquid not so rapidly changing. Tannic acid also precipitates solution of gelatine, and gallic does not.

(4) Take a good quantity of the neutralised and prepared solution, add excess of Fe_2Cl_6, filter out the precipitate and wash it. Now percolate it with some dilute NH_4HO, evaporate the liquid so obtained to a low bulk, cool thoroughly, and acidulate with HCl. **Benzoic acid** will separate in silky crystals, and succinic acid will not.

Step IV. If oleic, lactic, or sulphovinic (ethyl-sulphuric) acids be suspected, specially test for them as follows:—

Oleic acid will have shown its presence by always floating to the surface as an oily liquid whenever the prepared solution is acidulated with any acid. To confirm and distinguish it from the other fatty acids (stearic, etc.), take some of the prepared solution and acidulate with HCl, warm, and set aside till the oily layer floats up. Now remove the liquid beneath, as far as possible, with a pipette, add some water, boil, and drop in small fragments of K_2CO_3, until the oily layer is saponified and dissolves. Now put in a piece of test-paper and carefully add acetic acid to exact neutrality, then cool and precipitate with excess of $Pb(C_2H_3O_2)_2$. Filter out the oleate of lead, wash it with boiling water, let it thoroughly drain, and then prove that it is soluble in ether (stearate and palmitate of lead are insoluble).

Lactic acid. Acidulate the prepared solution with HCl and shake up with ether. Pipette off the ether into a porcelain capsule and let it evaporate at a *gentle* heat, when the acid will be left and may be recognised as follows: (*a*) A portion heated burns at first with a blue flame, and then the flame becomes luminous as the temperature rises. (*b*) Another portion warmed with $K_2Mn_2O_8$ gives the odour of aldehyd.

Sulphovinates do not precipitate $BaCl_2$ in the cold, but, on boiling, give a precipitate of $BaSO_4$ and an odour of spirit.

SOLUBILITY.

An important consideration before proceeding to the Acidulous Course.

Looking to the metals found, the question arises, what acidulous radicals could possibly be there, supposing the original substance to be soluble or insoluble in water or acids, or totally insoluble. Of the solubility of the commoner salts, the following table will show this, and a careful study of it will save much unnecessary and often misleading testing for acids. **The usual radicals are in words and the rarer ones in symbols bracketed.**

Metals found	If soluble in water, test for the following radicals.	If insoluble in water but soluble in acids, test for the following radicals.	If insoluble in acids, fuse with KNaCO$_3$, extract with H$_2$O, and test the solution for the following radicals.
Silver	Nitrate, Nitrite, Sulphate, Acetate (ClO, ClO_3, BrO_3, S_2O_3)	Oxide, Sulphide, Carbonate, Phosphate, Cyanide, Oxalate, Tartrate, Citrate (AsO_4, CrO_4, IO_3, S_2O_3)	Chloride, Iodide, Bromide
Mercury (ous)	Nitrate, Acetate, Sulphate (ClO, ClO_3, IO_3, BrO_3, NO_2, BO_3, $C_4H_4O_6$)	Oxide, Sulphide, Chloride, Iodide, Oxysulphate (PO_4, AsO_4, C_2O_4, CrO_4, $C_4H_4O_6$, $C_6H_5O_7$)	Chloride, Iodide, Bromide
Mercury (ic)	Chloride, Nitrate, Sulphate, Acetate (ClO, ClO_3, IO_3, BrO_3, Cy, S_2O_3, CrO_4, NO_2)	Oxide, Sulphide, Iodide, Carbonate, Oxysulphate (PO_4, C_2O_4, AsO_4, CrO_4, $C_4H_4O_6$)	Sulphide, Iodide
Lead	Acetate, Nitrate (Cl, I, ClO, ClO_3, BrO_3, NO_2, $C_6H_5O_7$)	Oxide, Sulphide, Carbonate, Phosphate, Oxalate (Cl, I, Cy, SO_3, S_2O_3, IO_3, BrO_3, AsO_4, CrO_4, $C_4H_4O_6$)	Sulphate, Chromate, Chloride, Iodide
Bismuth	Nitrate, Chloride, Sulphate, Acetate (Br, IO_3, BrO_3, ClO, ClO_3, S O_3, NO_2, $C_6H_5O_7$)	Oxynitrate, Oxychloride, Oxysulphate, Oxide, Sulphide, Carbonate, Phosphate (CrO_4, AsO_4, BO_3, C_2O_4, I, SO_3, $C_4H_4O_6$)	None
Copper (ic)	Chloride, Nitrate, Sulphate, Acetate (NO_2, ClO_3, S_2O_3, CrO_4, ClO, Br, IO_3, BrO_3, I, $C_4H_4O_6$, $C_6H_5O_7$)	Oxide, Sulphide, Carbonate, Phosphate, Arsenite, Oxyacetate (AsO_4, BO_3, Cy, SO_3)	„
Copper (ous)	Sulphate (Cl, Br)	Iodide (Cl, Br)	„
Cadmium	Chloride, Nitrate, Iodide, Sulphate (ClO, ClO_3, Br, IO_3, BrO_3, SO_3, S_2O_3, NO_2, $C_2H_3O_2$, $C_4H_4O_6$, $C_6H_5O_7$, BO_3)	Oxide, Sulphide, Carbonate, Phosphate (BO_3, C_2O_4, $C_4H_4O_6$)	„
Antimony	Chloride, Tartrate ($C_2H_3O_2$, C_2O_4)	Oxide, Sulphide, Oxychloride (SO_4, PO_4, CrO_4, I)	„
Tin (Stannous)	Chloride, Sulphate (ClO, ClO_3, Br, NO_3, NO_2, S_2O_3, $C_2H_3O_2$, $C_4H_4O_6$)	Oxide, Sulphide, Phosphate, Chromate (BO_3, C_2O_4)	„

Tin (Stannic)	Chloride (ClO_3, $C_4H_4O_6$, C_2O_4)	Oxide Sulphide (NO_3)	None
Gold	Chloride	Sulphide (Cy)	"
Platinum	Chloride	Sulphide	"
Iron (Ferrous)	Chloride, Sulphate, Iodide (see Ferric, also SO_3, S_2O_3)	Oxide, Sulphide, Carbonate, Phosphate, Arseniate (C_2O_4, BO_3, CrO_4, Cy, $C_4H_4O_6$, AsO_3)	"
Iron (Ferric)	Chloride, Nitrate, Sulphate, Acetate (Br, IO_3, BrO_3, ClO_3, NO_2, CrO_4, $C_4H_4O_6$)	Oxide, Sulphide, Iodide, Phosphate, Arseniate (C_2O_4 (when dried), BO_3, and SO_4 (and NO_3 when basic)	"
Aluminium	Like Iron	Like Iron	"
Cerium	Chloride	Oxide and Oxalate	Oxide
Chromium	Chloride, Sulphate, Acetate, Nitrate (Br, ClO, ClO_3, IO_3, BrO_3, S_2O_3, SO_3, C_2O_4, $C_4H_4O_6$, $C_6H_5O_7$)	Oxide, Phosphate Arseniate (BO_3, CrO_4, Cy)	Oxide
Manganese	Chloride, Sulphate, Acetate, Nitrate (Br, ClO, ClO_3, IO_3, BrO_3, SO_3, S_2O_3, NO_2, CrO_4)	Oxide, Sulphide, Carbonate, Phosphate (AsO_4, C_2O_4, BO_3, Cy, $C_4H_4O_6$, $C_6H_5O_7$)	None
Zinc	Chloride, Sulphate, Acetate, Nitrate (ClO, ClO_3, Br, IO_3, BrO_3, NO_2, S_2O_3, SO_3, CrO_4, $C_6H_5O_7$)	Oxide, Sulphide, Carbonate, Phosphate (C_2O_4, BO_3, AsO_4, Cy, $C_4H_4O_6$)	"
Nickel	Chloride, Nitrate, Sulphate, Acetate (ClO, ClO_3, IO_3, BrO_3, SO_3, S_2O_3, Br, NO_2)	Oxide, Sulphide, Carbonate, Phosphate (AsO_4, BO_3, CrO_4, Cy, $C_4H_4O_6$, $C_6H_5O_7$, C_2O_4)	"
Cobalt	Chloride, Nitrate, Sulphate, Acetate (ClO, ClO_3, IO_3, BrO_3, SO_3, S_2O_3, Br, NO_2, $C_6H_5O_7$)	Oxide, Sulphide, Carbonate, Phosphate (AsO_4, BO_3, CrO_4, C_2O_4, Cy)	"
Barium	Chloride, Nitrate, Acetate, Oxide (slightly) (ClO, ClO_3, I, Br, IO_3, BrO_3, S_2O_3, NO_2, Cy, $C_6H_5O_7$, S)	Carbonate, Phosphate, Oxalate, Chromate (O, AsO_4, BO_3, SO_3, $C_4H_4O_6$)	Sulphate
Strontium	Like Barium (except $C_6H_5O_7$)	Like Barium	Sulphate
Calcium	Like Barium (except $C_6H_5O_7$ soluble in cold but not in boiling water, $CaSO_4$ also slightly soluble)	Like Barium (except SO_3, which is soluble in H_2O and $CaSO_4$ slightly soluble)	Sulphate
Magnesium	Like Calcium	Like Calcium	None
Lithium	Oxide, Chloride, Sulphate	Carbonate, Phosphate, Oxalate	"
Potassium	All radicals form soluble salts *except* those mentioned opposite	$PtCl_4 2KCl$, $KHC_4H_4O_6$, and K_2SiF_6	"
Sodium	All radicals form soluble salts except	Sodium Antimoniate	"
Ammonium	Like Potassium		

NOTE.—When a radical is mentioned in more than one column, it means that it is so slightly soluble as to sometimes appear insoluble at first sight.

CHAPTER V.

QUALITATIVE DETECTION OF ALKALOIDS AND OTHER ORGANIC BODIES USED IN MEDICINE, TOGETHER WITH THE TESTING OF "SCALE PREPARATIONS" AND A GENERAL SKETCH OF TOXICOLOGICAL PROCEDURE.

DIVISION A. COURSE FOR THE DETECTION OF THE ALKALOIDS AND ALKALOID SALTS USED IN MEDICINE.

Note.—Aconitine is omitted because it can only be really detected by experiments upon animals. Salicine, acetanilide, and antipyrin, although not alkaloids, are included, as they give tests apt to be mistaken for certain alkaloids.

In this course not more than two definite *tests* for each alkaloid are recorded, and for the remaining tests the reader is referred to the full table facing p. 87.

Step I. Heat on platinum foil. If the substance at once takes fire and burns away with a smoky flame and an odour of singed hair, it is probably an alkaloid.

Step II. To a solution of the substance in water or dilute acid add:—

(*a*) *Mayer's solution* (see index), which gives a precipitate with all official alkaloids (except caffeine), but no effect with antipyrin.

(*b*) *Solution of potassium bismuthous iodide*,[*] which will give a precipitate with all official alkaloids, also with acetanilide and antipyrin.

Step III. Put a piece of red litmus paper on a watch-glass, lay on to this a little of the substance, and moisten it with a few drops of strong rectified spirit. If, on standing for a short time, the paper is rendered blue, we are dealing with a free alkaloid; if not, then it is an alkaloid salt, and in the latter case we shall have to search for the acid as well as the base.

Note.—Acetates of alkaloids often become basic and consequently alkaline by keeping, so beware of this.

Step IV. To a fragment of a substance on a watch-glass (placed over white paper) add a drop of strong H_2SO_4, and stir. A bright red **Salicine** and a deep red **Veratrine.**

Confirm former by warming with $H_2SO_4 + K_2Cr_2O_7$ = odour of *meadow-sweet* (salicylic aldehyde), and latter by its giving yellow with HNO_3 and blood-red on warming with HCl.

Note. Many alkaloids give pale dirty pinks with H_2SO_4, which are to be disregarded.

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[*] Made by mixing 43 c.c. of *liquor bismuthi* with 9 grms. of KI and 9 c.c. of strong hydrochloric acid.

Step V. To the liquid in which H_2SO_4 has given no distinct red add a small fragment of powdered ammonium molybdate, and stir.

(*a*) Greenish purple } = **Morphine** or **Apomorphine.**
Greenish black }

Confirm by adding HNO_3 to another fragment, when orange-red = morphine and blood-red = apomorphine. Morphine with Fe_2Cl_6 gives greenish blue, and apomorphine gives deep red. Morphine with $H_2SO_4 + Na_2HAsO_4$ = bluish green.

(*b*) Bright orange-red = **Brucine.**

Confirm by testing another fragment with HNO_3 and getting a bright red, turned to violet on warming with $SnCl_2$.

(*c*) Bright greenish blue = **Codeine.**

Confirm by adding HNO_3 to another portion. Pale evanescent yellow = codeine.

(*d*) A yellowish green = **Physostigmine.**

Confirm by adding HNO_3 to another portion. A strong gamboge yellow = physostigmine. Further confirm by getting a red with KHO, becoming blue on evaporating to dryness on the water-bath, and the residue dissolving in HCl to a dichroic solution.

(*e*) Evanescent green, changing to buff, with pale green streaks = **Hydrastinine.**

Confirm by testing with HNO_3 = pale yellow, becoming orange, and suddenly red on adding a drop of H_2SO_4.

Step VI. Treat another fragment with a drop of H_2SO_4 as before, then let another drop fall near it. Into the second drop put a fragment of powdered potassium bichromate, let it digest a moment, and then stir the drops together.

(*a*) Beautiful violet (evanescent) = **Strychnine** or **Acetanilide.**

To distinguish between these we test original substance with HNO_3, which gives no colour with strychnine, but a dirty yellow with acetanilide, turned red by NH_4HO. (Further confirmatory tests, see page 88.)

(*b*) An evanescent dirty red, following by pinkish buff and gradual formation of green streaks = **Cocaine.**

(1) Confirm by mixing 5 c.c. of a 2 per cent. solution with 5 drops of a 5 per cent. solution of chromic acid, and get a yellow precipitate, redissolving on shaking. Now add 1 c.c. HCl, and get a permanent orange-yellow precipitate.

(2) Moisten with HNO_3, dry and add a drop of alcoholic KHO, and get odour of peppermint.

Note.—A minute drop of a dilute solution of cocaine placed upon the tongue will cause tingling and numbness. (Aconitine, which also causes tingling in the tongue, gives a red crystalline precipitate with $K_2Mn_2O_8$ in the most dilute solutions (1 in 4000) acidulated with acetic acid, while cocaine does not, unless present in amounts over 1 per cent.

(*c*) A vivid emerald-green = **Pilocarpine.**

Confirm by testing with HNO_3 and getting a faint green.

(*d*) Faint yellowish greens more decided on standing = **Atropine, Caffeine, Hyoscine, Homatropine,** or **Hyoscyamine,** and indeed many alkaloids; but at this stage test only for the following, and if not found pass on to Step VII.

(1) *Atropine* warmed with H_2SO_4 gives a slightly roseate odour; on adding $K_2Cr_2O_7$ the odour suggests bitter almond oil. An alcoholic solution warmed with $HgCl_2$ gives yellow precipitate, turning red; with HNO_3 behaves like (3).

(2) *Caffeine* dissolved in a c.c. of HCl, a little $KClO_3$ added, and the whole evaporated to dryness on a water-bath, leaves a residue which becomes purple when exposed to the fumes of NH_3, which colour is destroyed by KHO.

(3) *Hyoscine* dissolved in HNO_3, and dried on water-bath, is turned violet by alcoholic KHO. An aqueous solution is precipitated by KHO, but not by NH_4HO.

(4) *Homatropine* similarly treated to hyoscine gives a *yellow* instead of a violet; shaken out from its salts with NH_4HO and chloroform, and the latter evaporated, leaves a residue, turned first yellow, and finally brick-red, with a 2 per cent. solution of $HgCl_2$ in diluted alcohol (proof spirit).

(5) *Hyoscyamine.* An aqueous solution acidulated with HCl is not precipitated by $PtCl_4$, but is by $AuCl_3$, and this, when dissolved in boiling H_2O, acidulated with HCl, and crystallised, yields lustrous golden-yellow scales (*distinction from atropine*).

Step VII. Dissolve some of the original substance in water (using a drop or two of acetic acid to help solution if necessary), then add chlorine water and a gradual excess of NH_4HO.

(*a*) A clear green solution = **Quinine** or **Quinidine.**

(*b*) A white precipitate = **Cinchonine, Cinchonidine,** or **Sparteine.**

(*c*) A clear yellow = **Phenazone** (*Antipyrin*). (Confirm by nitrite test, see page 90.)

Note.—In presence of salicylate the ordinary tests for quinine fail, and in this case it is necessary to dissolve in dilute hydrochloric acid, shake up with ether to remove salicylic acid, and then draw off the watery solution from beneath the ether and test it for quinine.

Separation of the Cinchona alkaloids from each other.—Dissolve in a little water by the aid of a few drops of dilute HCl, heat nearly to boiling and drop in dilute NaHO until the liquid is as nearly neutral as possible to litmus paper, and no more than a *mere trace* of permanent turbidity is produced; cool perfectly and then stir in saturated solution of Rochelle salt until precipitation ceases. When the precipitate has settled filter out the tartrates of **Quinine** and **Cinchonidine** so produced. To the filtrate add a little spirit, and stir in saturated solution of KI to precipitate the **Quinidine.** Again filter, add solution of ammonia in excess and shake up with a little ether, when **Cinchonine** will precipitate, and any *amorphous alkaloid* present will pass into the ether.

To separate Quinine and Cinchonidine.—Take the tartrates obtained as above, dissolve in a little water with sufficient HCl, place in a stoppered tube immersed in cold water, and then add sufficient ether, so that, after shaking and again coming to rest, there shall just be a visible layer of ether over the liquid in the tube. Now add excess of NaHO, again shake, cool, and see that a visible layer of ether still separates, but, should it not do so, a little more ether must be added and the whole once more shaken. The closed tube is now to be left in the cold for some time, and if the whole of the precipitated alkaloid remains dissolved in the ether, then it was all **Quinine,** but if a crystalline deposit forms at the base of the ether layers **Cinchonidine** is present.

To distinguish Sparteine from Cinchonine.—If 25 c.c. of ether be added to about 0·1 grm. of sparteine sulphate in a test-tube, then a few drops of dilute ammonia water, so that the latter shall not be in excess, and an ethereal solution of iodine (1 in 50) be afterwards added until the liquid, when shaken, turns from an orange to a dark reddish-brown colour, the bottom and sides of the test-tube will after a short time be found coated with minute, dark greenish-brown crystals, distinctly seen with a lens after the liquid has been poured out. (*U.S.P.*)

Step VIII. If we believe that we are dealing with an alkaloid salt we must now proceed to test the acid. The acid radicals usually present in alkaloidal salts of commerce are chloride, sulphate, acetate, phosphate, citrate, meconate, nitrate, and salicylate.

The first step will be to dissolve a little of the alkaloid salt in very dilute HNO_3, and test (1) for HBr with Cl water and chloroform; (2) for HCl by $AgNO_3$; (3) for H_2SO_4 by $BaCl_2$; (4) for H_3PO_4 by excess of ammonium molybdate and HNO_3.

The next will be to dissolve in water only, and test with Fe_2Cl_6 for acetate or meconate (red) or salicylate (violet). (Acetate decolourised by boiling, meconate not so; also acetate gives no precipitate with $Pb(C_2H_3O_2)_2$, and meconate does.)

Lastly, we must test in the usual way for a citrate (but, unless the base be caffeine, this is not likely), also for a nitrate (especially with pilocarpine and strychnine), and finally for a valerianate (with quinine).

KHO and a fragment of resorcin gives an intense red (*rosolic acid*); add a drop of aniline to some alcoholic solution of KHO, then add a drop or two of the suspected liquid and boil, when a fearfully offensive odour of phenyl-isocyanide is produced.

Creasote (chiefly guaiacol and creasol). Very slightly soluble in water, in which it sinks. The aqueous solution gives a green colour with ferric chloride, rapidly changing to a reddish-brown precipitate. Creasote is miscible with collodion without producing any turbidity, and it is insoluble in *commercial* glycerine (*distinction from liquid carbolic acid*).

Ethyl Alcohol. Add $K_2Cr_2O_7$ and H_2SO_4 and boil, and get a green colour and odour of aldehyd; heat with $NaC_2H_3O_2$ and H_2SO_4, and get odour of apples; warm with KHO and iodine, and get yellow precipitate of iodoform (*Leiben's test* best done on a portion that has been distilled off from the original liquid).

Glycerine. Colourless and odourless syrupy liquid, volatilising on heating with very irritating vapours. A borax bead dipped in glycerine and held in the *Bunsen* flame colours it green (if the original liquid be acid it must be first neutralised and ammonium salts must be absent). Two drops of concentrated glycerine heated to 125° C., with two drops each of phenol and H_2SO_4, yield a semi-solid mass which dissolves in dilute ammonia solution, giving a carmine colour. Before these tests are used for any mixture, it should be evaporated to dryness with excess of slaked lime at a temperature under 100° C., and the residue having been extracted with a mixture of equal volumes of absolute alcohol and ether, the resulting solution should be evaporated on a water-bath, and the tests applied to the residue.

Methyl Alcohol. To 5 c.c. of the liquid add 2 grammes of $K_2Cr_2O_7$, and 20 c.c. of dilute H_2SO_4 (1 in 4); let the whole stand for twenty minutes, and then distil off 10 c.c. Neutralise this distillate with Na_2CO_3, evaporate to a low bulk, acidulate with acetic acid, and apply the tests for *formate* (page 46).

Nitrobenzene (oil of mirbane). Yellowish oily liquid having an odour of bitter almonds. Placed in contact with zinc dust and diluted H_2SO_4, it is reduced to aniline. If a crystal of $KClO_3$ be dropped in and H_2SO_4 run down the tube (as in testing for nitrates) a violet colour is produced round the crystal.

Paraldehydum (paraldehyd). Soluble in water (1 in 10); miscible with ether; no colour with KHO after standing (*dist. from aldehyd*). Mirror on warming with ammonio-argentic nitrate.

II. *The substance is a solid* **which chars on heating and entirely burns away.** Observe the colour of the substance, try its solubility, first in cold water and then in cold chloroform, and apply the following:—

Case (A). Substance *white*, difficultly soluble (or insoluble) in *cold* water, but readily in chloroform. Suspect and test for:—

Acetanilide (antifebrin). Slightly soluble in cold water (neutral reaction); freely soluble in chloroform, ether, benzol, and rectified spirit. Heated with solution of KHO and a drop of chloroform, the odour of phenyl isonitrile is developed. Aqueous solution gives yellowish-white precipitate with bromine water (*distinctions from phenacetin*).

A cold solution gives no colour with Fe_2Cl_6 (*distinction from antipyrin, acetone, and aniline salts*). No colour with H_2SO_4.

Elaterin. In greenish-white friable masses. Insoluble in water, but soluble in chloroform. With a drop of liquefied carbolic acid and two drops of H_2SO_4 gives first crimson and then scarlet.

Naphtol (beta-naphthol). Often buff or yellow when old stock. Slightly soluble in water, freely in chloroform, and has a slight odour of phenol. Hot saturated solution with 1 drop of solution of NH_3 has a pale blue fluorescence. 0·1 grm. added to 5 c.c. aqueous KHO (1 in 4) with 1 c.c. chloroform, and gently warmed, the aqueous layer goes first blue, then green, and finally brown. 0·1 grm. in 10 c.c. boiling H_2O, mixed with 10 c.c. of 3 per cent. solution of Fe_2Cl_6, gives a precipitate becoming brown, but not violet (*absence of alpha-naphthol*).

Picrotoxinum (picrotoxin). Slightly soluble in water, freely in chloroform; soluble in 10 parts of a solution of KHO, and the liquid reduces Fehling's solution; H_2SO_4 gives a saffron-yellow; its solution is not precipitated by $HgCl_2$, by bismuth potassium iodide, $PtCl_4$, or by tannic acid (showing that it is not an alkaloid).

Salol (phenol salicylate). White crystalline powder. Almost insoluble in water, but freely in chloroform. On melting together salol and NaHO, and then rendering acid with HCl, crystals of salicylic acid separate, and the odour of phenol is obtained. If a few drops of very dilute Fe_2Cl_6 be added to 10 c.c. alcoholic solution of salol a violet is produced. Water that has been shaken with salol gives no colour with Fe_2Cl_6 (*absence of free salicylic acid*).

Santonin. White when fresh, pale yellow when old; nearly insoluble in water, soluble in alkali; added to a warm alcoholic solution of KHO gives a violet-red colour, gradually fading away; added to 1 c.c. of H_2SO_4 and a few drops of Fe_2Cl_6 and heated gives a red colour changing to brown. (*These will detect santonin in urine.*) Heated on a porcelain dish and H_2SO_4 added gives a purple.

Sulphonal. Slightly soluble in cold water and in chloroform; fused with an equal weight of KCN the odour of mercaptan is evolved, and the residue dissolved in water, acidulated with HCl and Fe_2Cl_6 added, a red colour is produced; a solution mixed with 4 drops of carbolic acid, and strong H_2SO_4 added till the liquid boils, a green colour is obtained. Heated in air gives off SO_2, or with dried $NaC_2H_3O_2$ gives H_2S.

Case (*B*). Substance *white*, not readily soluble in cold water or cold chloroform. Suspect and test for:—

Glusidum (saccharine or benzoyl-sulphonic imide). Not readily soluble in cold water or in chloroform; heated to redness with Na_2CO_3 it chars and gives off an odour of benzene; not blackened by H_2SO_4; on fusing with NaHO, cooling, dissolving in water, faintly acidulating with HCl, and adding Fe_2Cl_6, a reddish purple is obtained.

Phenacetinum (phenacetin). Only slightly soluble in cold water, and not freely in chloroform. A hot solution gives a violet with chlorine water, fading to red; boiled with HCl and Fe_2Cl_6 added gives a red; mixed with four drops of carbolic acid, and H_2SO_4 added till the liquid boils, gives a purplish-brown colour and odour of acetone; 0·1 grm. boiled with 2 c.c. of HCl for

½ minute, and the liquid diluted with 10 volumes of water, cooled and filtered, gives a deep red with solution of chromic acid; does not give precipitate with bromine water, nor does it give the isonitrile test (*dist. from acetanilide*). 0·3 grm. in 1 c.c. 90 per cent. alcohol, diluted with 3 c.c. water and boiled with 1 drop $\frac{N}{10}$ iodine solution, gives no red (*absence of paraphenetidin*).

Case (*C*). Substance *white* (crystalline), and readily soluble in cold water. Suspect and test for:—

Chloral (*hydrous*). Soluble in water. Heated with solution of KHO gives odour of chloroform, and the contents of the tube give the reactions of a formate (page 46). Gives the same test with resorcin as chloroform. Mixed with a 5 per cent. solution of carbolic acid, and an equal bulk of H_2SO_4 added, gives a pink.

Phenazonum (antipyrin or phenyl-methyl-pyrazolone). Freely soluble both in water and chloroform; with $NaNO_2$ and diluted sulphuric acid gives a green; an aqueous solution with an equal volume of HNO_3 is yellow, passing to crimson on warming; Fe_2Cl_6 gives a deep red, discharged by dilute H_2SO_4. 2 c.c. of a 1 per cent. aqueous solution with 2 drops of HNO_3 goes green, changed to red by adding 3 drops more and boiling.

Resorcin. Freely soluble in water; Fe_2Cl_6 added to an aqueous solution gives violet, discharged by NH_4HO; Na_2OCl_2 gives a violet, fading to yellow; NH_4HO and $CaOCl_2$ gives a red violet, turning yellow.

Soluble Saccharine. Tests as for glusidum, but when heated to redness leaves a residue giving the tests for sodium.

Sugars. (*a*) *Sucrose* (cane sugar). A solution boiled with *dilute* H_2SO_4 darkens markedly, but not when boiled with *liquor potassæ*. Trommer's test (a few drops of solution of $CuSO_4$ with an excess of KHO and boiled) gives no red. Fehling's solution (see p. 129) gives no red.

(*b*) *Glucose* (grape sugar). A solution gives no darkening when boiled with *dilute* H_2SO_4, but darkens when boiled with *liquor potassæ*. Trommer's and Fehling's tests both give a red precipitate.

(*c*) *Lactose* (milk sugar). A solution is only slightly affected either by boiling with dilute H_2SO_4 or with *liquor potassæ*. Fehling's and Trommer's tests both give a red precipitate.

Case (*D*). The substance is coloured. Suspect and test for:—

Adeps Lanæ (cholesterin-fat). Insoluble in water, soluble in chloroform and ether, sparingly in rectified spirit. The chloroformic solution poured gently over the surface of strong H_2SO_4 gives a purple; five grammes in ethereal solution mixed with phenolphthalein give a red on the addition of ·2 c.c. of normal sodium hydrate (*distinction from ordinary fatty acids, which would saponify and absorb much more soda*). Soluble in boiling alcohol, and crystallises out on cooling.

Aloin. Yellow and slightly soluble in cold water, freely in hot; insoluble in ether. HNO_3 gives a red (except with socaloin, which goes brownish). Dissolve in strong H_2SO_4 and a few drops HNO_3, dilute with water, and get a yellow, turned deep claret by excess of NH_4HO. H_2SO_4 on a fragment of aloin, and a rod moistened with HNO_3 held near, gives a blue with nataloin only.

Chrysarobin. A brownish-yellow powder, partly volatile by heat with yellow vapours; insoluble in water, but soluble in KHO, gradually producing a brilliant red. H_2SO_4 on the fragment gives a reddish brown.

Fel Bovinum (ox bile). Yellowish-green substance, soluble in water and spirit. A solution mixed with a drop of syrup and then H_2SO_4 cautiously added becomes cherry-red, changing successively to carmine, purple, and violet.

Gelatinum (gelatine). Swells up in water, soluble on boiling. Tannic acid gives a flocculent precipitate; $HgCl_2$ gives a white; not precipitated by dilute acids, alum, plumbic acetate, or ferric chloride.

Guaiacum Resin. In powder yellowish green. Insoluble in H_2O, but soluble in alcohol, and this solution becomes blue with Fe_2Cl_6 or solution of H_2O_2. The $H_2SO_4 + H_2O$ test (see Jalap Resin) gives a characteristic odour somewhat balsamic.

Iodoform. Yellow, insoluble in water, and characteristic odour; warmed with alcoholic solution of KHO, and then mixed with starch paste and excess of HNO_3, gives a blue. (May be detected in urine by adding alcohol and pouring upon phenol-potassium contained in a test-tube, when the red colour will cover the bottom of the tube; soluble in alcohol.)

Jalap Resin. Dark brown in fragments, paler in powder. Insoluble in water, but soluble in alcohol; insoluble in turpentine. H_2SO_4 dropped on a fragment turns it reddish, and on adding a few drops of water, so as to cause evolution of steam, the characteristic odour of jalap is observed. Only 10 per cent. should be soluble in ether (*absence of scammony or Tampico jalap resins*).

Podophyllin. Pale yellow to orange-brown. Insoluble in water, but soluble in spirit; soluble in NH_4HO; H_2SO_4 on a fragment slightly colours it, and on adding a drop or two of water no characteristic odour is evolved. Partly soluble in ether.

Resin. Insoluble in water, soluble in alcohol and in turpentine; H_2SO_4 on a fragment gives a strong red, and on adding a few drops of water, so as to cause evolution of steam, the characteristic odour is observed.

Scammony Resin. Brownish translucent fragments. Insoluble in H_2O, but soluble in alcohol, and completely in ether (*distinction from jalap resin*). Alcoholic solution gives no colour with Fe_2Cl_6 or H_2O_2 (*absence of guaiacum resin*). The $H_2SO_4 + H_2O$ test gives the odour of scammony.

DIVISION C. QUALITATIVE ANALYSIS OF SCALE PREPARATIONS.

Step I. Heat a little to redness on platinum foil, and observe the following possible cases:—

(*a*) If it entirely burns suspect **Beberine sulphate.**

Confirm by testing for sulphate by $BaCl_2$; and for beberine with KHO, getting a yellowish-white precipitate entirely dissolved by agitating the liquid with twice its volume of ether. This ethereal liquid evaporated leaves a yellow residue entirely insoluble in dilute HCl.

(*b*) An ash is left: (a) Put a small fragment of the ash upon a piece of red litmus paper, moisten it with a drop of water, and, if it turns the paper blue, suspect **potassium**; (b) Dissolve the remainder of the ash in nitric acid, dilute and test with excess of ammonium molybdate for **phosphoric** acid.

Note.—If K be suspected, prove it by igniting some more of the scale, extracting the ash with very little boiling water, filtering, cooling, and adding $PtCl_4$.

Step II. Make a weak solution of the scale, acidulate it with a drop of HCl, and test for **ferrous** iron with $K_4Fe_2C_{12}N_{12}$, and for **ferric** with $K_4FeC_6N_6$. Also test another portion by adding excess of $AgNO_3$, and heating, when reduction to black or a mirror = **tartrate.**

Step III. To a strong solution add excess of NaHO, boil, and smell for **ammonia.** If neither phosphoric nor tartaric acid has been already found, filter out the precipitated ferric hydrate and use the filtrate for testing for acids as follows:—

(*a*) Test a portion for citric acid exactly as directed in the organic acid course (page 80).

(*b*) Test another portion by exactly neutralising with HNO_3, and adding $AgNO_3$, when a white precipitate = **pyrophosphate,** and the same turning black = **hypophosphite.**

Of course this step is never to be taken unless an indication of P be got in the ash with molybdate in Step I.

Step IV. Make a solution of a fair amount of the scale, add a drop or two of very dilute NH_4HO, and then add some strong NH_4HO.

Case (*A*). There is either no precipitate, or it dissolves in strong NH_4HO: Add some chloroform and shake up. Separate the chloroform by a pipette, and evaporate it to dryness in two portions on separate white dishes. Test the one residue for **strychnine,** and the other for **quinine.**

Case (*B*). The NH_4HO causes a permanent white precipitate: Filter out precipitate, and dissolve it off the filter with a little warm water containing a few drops of acetic acid. Boil the solution down to a low bulk, cool, neutralise if necessary with very dilute NaHO, and then add a few drops of saturated solution of Rochelle salts and shake, when a white precipitate = **cinchonidine.** If not that, then add NH_4HO, when a white precipitate insoluble on shaking with ether = **cinchonine.**

DIVISION D. GENERAL SKETCH OF THE METHOD OF TESTING FOR POISONS IN MIXTURES.

This course is only carried down to the best method of preliminary procedure for the *isolation* of the poison, all the individual tests to be afterwards applied having been already fully described in this or former chapters.

Note. Students desiring to study the subject more deeply are referred to Dr. Leyda's articles on detection of poisons in the *Analyst* for 1890.

Step I. If the liquid be very strongly acid, and effervesces violently with $NaHCO_3$, test for poisonous acids, specially for **Nitric and Oxalic.**

Note. Oxalic acid is best separated from a mixture by precipitation with plumbic acetate, filtering, suspending the precipitate in water, and passing H_2S. This removes the lead, and, after again filtering out the PbS, the liquid is evaporated to a suitable bulk and tested for oxalic acid.

Step II. Acidulate with $\frac{1}{4}$ of its bulk of HCl (filter, if necessary), and apply Reinch's test for As, Sb, Hg.

Step III. Burn to ash, dissolve this in HCl or HNO_3, and test by ordinary course for poisonous metals, especially Pb, Cu, and Zn.

Step IV. If the original, either alone or when heated with dilute H_2SO_4, gives the odour of HCN, of carbolic acid, or of phosphorus, test specially for them.

The reactions of HCN have been given at page 40, while those of carbolic acid are found at page 51. If a piece of filter paper, moistened with solution of $AgNO_3$, and suspended in the neck of the flask or bottle containing the suspected matter, be not darkened after warming the whole to 50° C. for a short time, no phosphorus is there. If darkening should occur, the suspected matter is to be acidulated with H_2SO_4, and distilled in a dark room, using a glass Liebig's condenser, when a luminous ring will be observed to form in the upper part of the condenser tube. If the suspected matter should contain spirit or certain other volatile bodies, the ring will not appear till they have passed over.

Step V. *If the original has no odour of opium* we proceed to apply Stas's process for the detection of alkaloids as follows:—

If the original be a solid, it is operated upon directly, but, if a fluid, it is first evaporated to dryness on a water-bath. Add some strong alcohol and a small crystal of tartaric acid, boil, and filter. Evaporate the filtrate to dryness on the water-bath, and take up with warm water slightly acidified with acetic acid, then cool and filter (if necessary), taking care that the liquid just remains acid. Put this acid liquid into a separator (fig. 17), and shake it up with ether or benzene, and carefully separate the ether. (This ether may contain fat, certain bitter principles, and glucosides, and therefore, in a general investigation of a drug, it should not be rejected, but evaporated, and the residue examined.) Now make the liquid distinctly alkaline by the careful addition of Na_2CO_3 or NaHO, and again shake up in the separator with chloroform, which will take up all the alkaloids except morphine. The chloroform is separated, evaporated at a very gentle heat, and the residue tested for alkaloids by the course given in Division A by the table facing page 87 of this chapter. Lastly, the alkaline liquid is shaken up with warm amylic alcohol, which extracts morphine and leaves it upon evaporation.

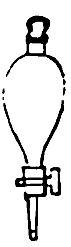

Fig. 17.

Note.—It is often better to get the alkaloids out from the chloroform or amylic alcohol by shaking the separated solvent up with water acidulated with acetic acid or HCl, thus getting an aqueous solution of the alkaloid and leaving any resinous matters in the chloroform. The re-treatment of this solution with alkali and chloroform, etc., will then enable us to get the alkaloid in a state of purity.

Step VI. *When opium is suspected.* Acidulate with acetic acid and filter, if necessary (any alcohol present being got rid of by boiling it off). Precipitate when cold with solution of plumbic acetate, filter, and preserve the precipitate (A) for examination for meconic acid and the filtrate (B) for morphine.

(*a*) Precipitate (A) is suspended in water and treated with H_2S till perfectly decomposed; the PbS filtered out, and the filtrate, after evaporation to drive off H_2S, tested for **meconic** acid. If this be found, it is held to be sufficient proof of presence of opium taken in connection with the odour of the original.

(*b*) Filtrate freed from Pb by H_2S and filtering is evaporated to dryness with a slight excess of $NaHCO_3$ on a water-bath. The residue will yield its **morphine** to alcohol, generally in a state sufficiently pure to evaporate a drop, and test. If not, then amylic alcohol must be used.

PART II.

QUANTITATIVE ANALYSIS.

CHAPTER VI.

WEIGHING, MEASURING, AND SPECIFIC GRAVITY.

I. WEIGHING AND MEASURING.

All bodies mutually attract each other. As the earth is the largest body within our atmosphere, it follows that its attraction is always greater than that of any surrounding matter. The force thus developed is called the attraction of gravitation, and its exercise is the cause of weight. Weighing is performed by means of the well-known appliance called the **balance**. Figure 18 illustrates a chemical balance of the modern short-beam type. H is the handle by which the balance is put into action, and R is the appliance for placing rider weights upon the graduated beam. Weights are made either according to the metrical or the English system, as follows:—

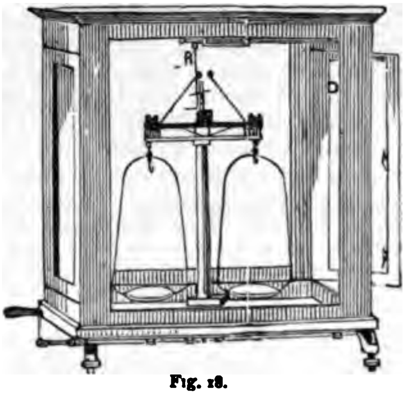

Fig. 18.

(*a*) *The Metrical system.*—The metrical weights of precision above one gramme are in brass; and then we have ·5, ·2, ·1, ·1, and following them .05, ·02, ·01, ·01, all in platinum or aluminium foil. The quantities below ·01 (one centigramme) are weighed by a rider on the beam. The combination of 5, 2, 1, and 1 has been chosen because they have been found to give the greatest number of possible combinations with the fewest weights. Figure 19 shows such a box of metrical weights as usually employed in quantitative analysis. The metrical system is founded upon the ***mètre***. The metre is multiplied and divided entirely by 10, thus:—

Fig. 19.

Kilo-metre	1000·
Hecto-metre	100·
Deca-metre	10·
Metre	1·
Deci-metre	·1
Centi-metre	·01
Milli-metre	·001

The metre taking the practical place of the English yard, the decimetre consequently takes the place of the foot, and the centimetre of the inch; and just as weight is got in our system from the cubic inch, so it is got metrically from the cubic centimetre, only much more simply, because 1 *cubic centimetre of distilled water, measured at 4° C. and 760 millimetres bar., weighs one gramme.* The gramme is multiplied and divided exactly as the metre, thus:—

Kilo-gramme	1000·
Hecto-gramme	100·
Deca-gramme	10·
Gramme	1·
Deci-gramme	·1
Centi-gramme	·01
Milli-gramme	·001

One kilogramme (1000 grammes) of water at the standard temperature and pressure measures one litre (or 1000 cubic centimetres), and we have therefore the following simple relation of weights and measures of water:—

Weight.	Measure.
1000 grammes	1 litre or 1000 cubic centimetres.
100 „	1 deci-litre or 100 „ „
10 „	1 centi-litre or 10 „ „
1 gramme	1 milli-litre or 1 cubic centimetre.

So we see that using water at 4° C., a gramme by weight and a cubic centimetre by measure amount to the same thing; as likewise do a kilogramme by weight and a cubic decimetre (or litre) by measure. The relation between the two systems is easily calculated from the following standards:—

Metrical.		English.
1 Gramme	=	15·432 grains.
1 Kilogramme	=	2·205 lb. (or 15,432 grains).
1 Litre	=	1·76 pints (or 35 fl. oz., 2 drachms, 11 minims).
1 Metre	=	39·37 inches.

So that 1 decimetre is, as nearly as possible, 4 inches; and 1 decilitre, a trifle under 4 fluid ounces.

(*b*) *The English system.*—In weights of precision, any amount above 10 grains is usually represented by a series of small brass cylinders, from 10 to 1000 grains; then follow 6, 3, 3, 2, and 1 grain in platinum wire, and afterwards ·6, ·3, ·3, ·2, and ·1 of a grain in platinum, or, more frequently, in aluminium wire. Quantities of less than $\frac{1}{10}$ grain are weighed by a small rider of gold wire placed on the beam of the balance. The foundation of the English system is the inch. One cubic inch of distilled water, measured at 60° F. and 30 inches barometrical pressure, weighs 252·45 grains, or 252½ grains nearly. There are 437·5 grains in an ounce, and 16 ounces (or 7000 grains) in a pound. Measure of capacity is obtained by weighing out 10 lb. of water at 60° F. and 30 inches bar., when the whole measures one gallon. The gallon is in turn divided into 8 pints (= 20 ounces, or 8750 grains of water, per pint); the pint into 20 fluid ounces (= 437·5 grains of water per fluid ounce); the fluid ounce is divided into 8 fluid drachms (= 54·68 grains of water per fluid drachm); and, lastly, the fluid drachm is divided into 60 minims (·91 grain of water in each minim).

II. SPECIFIC GRAVITY

may be generally explained to be the ratio of the weight of one thing to the weight of an equal volume of something else taken as a standard. For liquids and solids the standard is distilled water at a temperature of 60° F. An acquaintance with the various cases which may occur in the taking of specific gravity is of great importance, as it forms an exceedingly ready method of testing the purity and strength of many substances. A knowledge of the specific gravity of the various bodies also enables the chemist to tell at once what any given volume of a liquid ought to weigh, or conversely, what size of vessel will be required to contain any given weight. The following are the chief varieties of cases which may occur in taking :—

(*A*) Specific Gravity of Liquids.

CASE 1. **To take the specific gravity of a fluid.**—A small bottle of thin glass is procured, and counterpoised upon a balance. It is then filled with distilled water at 15·5° C. (60° F.), and the weight of the water thus introduced noted. The bottle, having been emptied and dried, is filled with the liquid to be tested, also at 15·5° C. (60° F.), and the whole is again weighed. By this means, having ascertained the weight of equal bulks of water and fluid, it only remains to divide the weight of the fluid by the weight of the water, and the quotient will be the specific gravity required. To make the calculation clear, observe the following examples :—

A counterpoised bottle filled with distilled water weighs 100 grammes ; the same bottle filled with sulphuric acid weighs 184·3 grammes, then :

$$\frac{184\cdot3}{100} = 1\cdot843, \text{ the specific gravity of the acid.}$$

Again, the same bottle, carefully washed, and filled with rectified spirit, weighs 83·8 grammes, then :—

$$\frac{83\cdot8}{100} = \cdot838, \text{ the specific gravity of rectified spirit.}$$

In practice, bottles are sold with perforated stoppers, which, when entirely filled with the liquid, and the stopper dropped in, so that no bubbles of air are allowed to remain between the stopper and the liquid, exactly hold a given weight of water. A counterpoising weight for the empty bottle is also provided ; so that there is nothing further to be done but simply to place the counterpoise in one scale, and the bottle, filled with the liquid under examination, in the other ; and having ascertained the weight, to divide by the known weight of water for which the bottle was constructed. Fig. 20 shows an ordinary specific gravity bottle. Fig. 21 shows a specific-gravity bottle the stopper of which is a thermometer, thus enabling us to observe the exact temperature of the liquid at the moment of weighing.

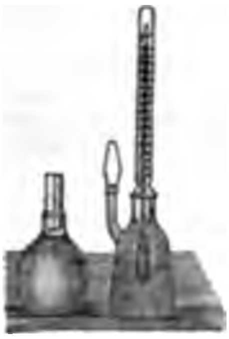

Fig. 20. Fig. 21.

CASE 2. **To take the specific gravity of a liquid by means of the hydrometer.** The hydrometer depends for its action on the theorem of Archimedes. If a solid body be immersed in a liquid specifically heavier than itself, it continues to sink until it has displaced a bulk of fluid equal to its own weight, and then it becomes stationary. Suppose an elongated body with a weight at its base to cause it to float upright, which has a specific weight exactly half that of water, be immersed in that fluid, it will sink to exactly half its length, because its whole weight is counterpoised by a bulk of fluid equal to half its size. A hydrometer is a long narrow glass or metal tube with a bulb near the bottom filled with air, and another smaller bulb beneath containing a sufficient quantity of mercury to weight it and cause it to float upright. There are two kinds of hydrometers: (1) for fluids heavier than water, and (2) for fluids lighter than water. The graduation of the former is performed by immersing the instrument in water and introducing such a quantity of mercury as will cause it to sink, so that only about one inch remains unsubmerged, and marking this point 1. The instrument is then plunged successively into several liquids heavier than water, the specific gravities of which are known, and the points to which it rises are marked and numbered. By this means a scale can be made between those points indicating any gravity from 1 upwards. In hydrometers for fluids lighter than water, the first sinking in that liquid is continued by weighing until only the upper bulb is immersed; and this point having been marked 1, the instrument is placed successively in known fluids lighter than water, the points to which it sinks marked, and by this means a whole scale is obtained. The method of using the hydrometer is readily seen from the illustration (fig. 22), in which A is the hydrometer, and B is a thermometer also placed in the liquid to show the temperature. Most hydrometers being made to indicate specific gravity at 15·5° C. (60° F.), it follows that the liquid must either be first brought to that temperature before using the instrument, or else the temperature employed must be noted, and a calculation made, based upon the coefficient of expansion of the liquid in question.

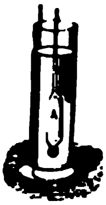

Fig. 22.

Syke's hydrometer is used in England by the officers of excise, to indicate the strength of spirituous liquors, and thus facilitate the collection of the revenue. It is a short brass instrument with the stem graduated from 0 to 10, and a series of nine weights to place beneath the bulb. By observing (1) the temperature, (2) the weight put on, and (3) the point to which it sinks on the stem, and referring to a book of tables which is sold with the hydrometer, the strength of the spirit is ascertained. Another modification of the instrument is found in *Twaddell's* hydrometer, which is used in chemical works for testing the density of liquids having a greater specific gravity than water. It is so graduated that the reading of any indicated degree, multiplied by 5 and added to 1000, gives the specific gravity as compared with water. Specific gravity beads form the only other variation of the hydrometric idea. These are small loaded bulbs of known specific gravities, which are thrown into the liquid to be tested, when the number marked upon the bead, which just floats underneath the surface and shows no tendency to sink or rise, gives the specific gravity required. Hydrometers in any form must in accuracy rank considerably beneath that of the specific gravity bottle; but in commercial operations, where an approximation only to correctness is required, these little instruments are invaluable.

CASE 3. **To take the specific gravity of a liquid by weighing a solid body in it.**—Take the weight of a glass stopper, or other suitable plummet, by suspending it from the hook provided for the purpose in all balances of modern type (see fig. 18, page 94). Put a wooden stool (also provided with all modern balances) over the pan, and upon this place a beaker containing distilled water at 15·5° C. (60° F.). Let the plummet hang beneath the surface of the water and again weigh, and then empty out the water, substitute the fluid (also at 15·5° C. (60° F.)), immerse the plummet as before, and once more weigh. By deducting respectively the weights in water and in fluid from the weight in air, we get the loss of weight sustained by the plummet in each case. It is evident that the lighter the liquid, the more the plummet will weigh; therefore we *divide the loss of weight in the fluid by the loss of weight in water*, which will give the specific gravity of the liquid. This rule is now practically applied in all modern laboratories by means of the **Westphal**

balance (fig. 23). By this a small thermometer (A), adjusted to a counterbalancing weight (B), is placed in the liquid, and the loss of weight is restored by little rider weights placed on the beam, which are so contrived as to readily indicate the specific gravity without calculation.

(*B*) Specific Gravity of Solids.

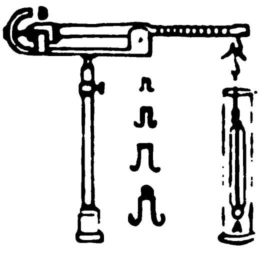

Fig. 23.

CASE 1. **To take the specific gravity of a solid body in mass which is insoluble in and heavier than water.**—The method by which this process is conducted was suggested by a theorem attributed to Archimedes, which may be thus expressed:—A solid on being immersed in a liquid is buoyed up in proportion to the weight of the fluid which it displaces, and the weight it thus apparently loses is equal to that of its own bulk of the liquid. A piece of the solid substance to be tested is weighed, and is suspended by means of a fine thread from one arm of a balance so that it dips under the surface of a vessel containing distilled water at 15·5° C. (60° F.), when its weight is again noted. Its weight in water is deducted from its weight in air, and the weight in air is divided by the difference so obtained, which gives the specific gravity.

EXAMPLE.

A piece of marble weighs	30	grammes.
Immersed in distilled water	18·89	,,
Difference in weight	11·11	,,

By dividing 30 by 11·11 we obtain the quotient 2·7, which is the specific gravity of the marble. The practical arrangement has been already described above (*Liquids, Case 3*).

CASE 2. **To arrive at the specific gravity of a powder which is insoluble in and heavier than water.**—Weigh a portion of the powder in air, then introduce it into a counterpoised specific gravity bottle constructed to hold a known weight of water. Let the bottle be carefully filled with distilled water, gently agitating to insure that no minute bubbles of air shall remain attached to the particles of powder; then weigh the whole. From the weight of the powder in air, *plus* the known weight of water which the bottle should contain, deduct the weight obtained in the second operation, and divide the original weight of the powder by this difference.

EXAMPLE. 2 grammes of a powder are weighed out, and poured into a counterpoised specific gravity bottle, constructed to hold 100 grammes of water. The bottle thus charged is found to weigh 101·2 grammes: then—

2 grammes + 100 grammes =	102	grammes.
Weight of the bottle when charged with powder and water .	101·2	,,
Difference .	8	,,

Therefore, 2 grammes divided by ·8 gramme will give 2·5 as the specific gravity of the powder.

CASE 3. **To take the specific gravity of a substance in mass, insoluble in, but lighter than, water.**—The difficulty met with in this case consists in the impossibility of weighing such a substance alone in water, because it floats on the surface of that liquid. It therefore becomes necessary to attach a piece of lead sufficiently heavy to sink it, and thus a complication is introduced. The light substance is first weighed in air in the ordinary manner, and is then attached to a sinker, and suspended from one arm of a balance under the surface of distilled water, when the combined weight of both is ascertained.

The light body is now detached, and the weight of the sinker alone in water noted. By these means we obtain the following data:—

i. The weight of the light body in air.
ii. The weight of the sinker in water.
iii. The weight conjointly of the light body and sinker in water.

We then deduct the weight of both in water from the weight of the sinker in water; add the weight of the light substance in air; and divide the weight of the light body in air by the product so obtained.

Example.—A light substance weighs 12 grammes in air; being attached to a piece of lead and weighed in distilled water the united weight amounts to 4 grammes, while the weight of the lead alone in water shows 5 grammes. Then:—

Weight of lead in water . . .	5	grammes.
Weight of both in water . . .	4	,,
Difference	1	gramme.
Add weight of light body in air . .	12	grammes.
Sum	13	,,

Dividing 12, the weight in air, by 13 obtained as above, we arrive at the decimal fraction ·923 as the specific gravity of the light substance tested.

Case 4. **To obtain the specific gravity of a substance soluble in water.**—Proceed exactly in the same manner as in Case 2 or 3, according as the body is in mass or in powder; but instead of water, use oil of turpentine or some other liquid in which the solid is insoluble. Having obtained the specific gravity of the substance by calculating just as if water had been used, multiply the result by the known specific gravity of the oil of turpentine or other fluid employed.

Example.—A lump of sugar weighing 10 grammes was found to weigh when immersed in oil of turpentine 4·562 grammes. Then—

The weight of the sugar in air was . . .	10	grammes.
,, ,, oil of turpentine .	4·562	,,
Difference	5·438	,,

Dividing 10 grammes by 5·438 grammes yields 1·84 as the specific gravity, as if water had been used; and by multiplying this result by ·87, the specific gravity of oil of turpentine, we obtain 1·6 as the actual specific gravity of the sample of sugar operated on.

Having thus considered in detail the various complications which may arise in taking the specific gravity of liquids and solids, it only remains to point out how the foregoing may be rendered subservient to commercial purposes.

(*C*) Practical Applications of Specific Gravity of Solids and Liquids.

Case 1. **The specific gravity of a body being known, it is desired to ascertain the weight of any given volume of the substance.** Find the weight of the given bulk considered as water, and multiply this amount by the specific gravity.

Example i.—What would be the weight of a fluid ounce of oil of vitriol? We know that a fluid ounce of distilled water weighs 437·5 grains, and the specific gravity of oil of vitriol is 1·843; so, if we multiply the former figures by the latter, we obtain 806·31 grains, which is the weight of a fluid ounce of this acid.

Example ii.—How much should a litre of chloroform weigh? The weight of a litre of water is 1000 grammes; and by multiplying 1000 by 1·49, the specific gravity of the chloroform, we obtain 1490 grammes, as an answer to the question.

Example iii.—How much should a fluid ounce of pure ether weigh? The specific gravity is ·72, and a fluid ounce of distilled water weighs 437·5 grains; multiplying the one number by the other gives 315 grains.

CASE 2. **Given the weight of any known bulk of a liquid, to find its specific gravity.**—Divide the weight by that of the given bulk considered as distilled water.

EXAMPLE.—A pint of spirit weighs 16¾ ounces. Is it rectified or proof spirit? By dividing this weight by 20 ounces, the ascertained weight of a pint of distilled water, we obtain as an answer ·838. We know, therefore, that the spirit thus tested must have been rectified.

CASE 3. **To find the amount of solid matter, in grammes, present in 100 c.c. of a solution of given specific gravity.** So far as any ordinary rule can be laid down, especially with regard to saccharine liquids, for which this calculation is generally used, we multiply the gravity by 1000, and then, having deducted 1000 from the product, we divide by 3·85.

EXAMPLE. A saccharine solution has a gravity of 1·0114: how much solid matter in grammes does it contain in each c.c.?

$$1{\cdot}0114 \times 1000 = 1011{\cdot}4 - 1000 = 11{\cdot}4 \therefore \frac{11{\cdot}4}{3{\cdot}85} = 2{\cdot}961 \text{ grammes per 100 c.c.}$$

(*D*) Specific Gravity of Gases.

Taking the density of gases and vapours involves many more complicated considerations than are required in the methods applicable to the specific gravity of liquids and solids. The standard adopted for such bodies is hydrogen, measured at a temperature of 0° C. and a barometrical pressure of 760 millimetres (N.T.P.).

When taking the specific gravity of liquids or solids, it is easy to obtain the water or other fluid required at the exact temperature necessary, by the use of cooling or heating appliances. With a gas we need exercise no such manipulation, because the coefficient of expansion of all vapours and gases is alike and well ascertained. The measurement of gases is therefore conducted without any attempt to modify these conditions; but the indication of the thermometer and barometer being carefully noted at the time of the experiment, a simple series of calculations enables us to ascertain how much the volume of gas would have measured had the test been conducted at a standard of temperature and pressure. The following are specimens of such calculations:—

Correction of the volume of a gas for changes of temperature.—This is based on Charles' law, which states that "the volume occupied by any given weight of a gas is directly proportional to its absolute temperature." *Absolute temperature* means degrees above 273° C., which is the absolute zero of temperature. To convert degrees of ordinary temperature into absolute degrees, it is therefore necessary to add 273 to all degrees above zero, while degrees below 0° are to be deducted from 273. From this law, given—v, the volume; v', the required volume; t, the given *absolute* temperature; and t', the required absolute temperature;—we employ the following calculations:—

$$\frac{t' \times v}{t} = v', \text{ and } \frac{v' \times t}{v} = t'.$$

Correction of the volume of a gas for changes of pressure.—The law of Boyle states that "the volume occupied by any given weight of a gas is inversely proportional to the pressure." Therefore, p being the given pressure, and p' the required pressure, we have

$$\frac{p \times v}{p'} = v', \text{ and } \frac{v \times p}{v'} = p'$$

When a gas is measured it is generally necessary to correct for both conditions, and then we employ double proportion. The following formulæ will be found useful as meeting all ordinary cases:—

(1) *Wanted the change of volume resulting from a given alteration of temperature and pressure:—*

$$\frac{p \times t' \times v}{p' \times t} = v'.$$

(2) *Wanted the change of temperature resulting from a given alteration of volume and pressure:—*

$$\frac{p' \times v' \times t}{p \times v} = t'.$$

(3) *Wanted the change of pressure resulting from a given alteration of volume and temperature:—*

$$\frac{v \times t' \times p}{v' \times t} = p'.$$

(4) To find the volume at N.T.P. of any gas measured at a given temperature and pressure (the temperature being above 0°):—

$$\frac{p \times 273 \times v}{p' \times (273 + \text{given temp.})} = v'.$$

Or, in a decimal fraction (*dt* = difference between 0° and given temperature):—

$$\frac{p \times v}{p' \times (1 + \cdot 003665\, dt)} = v'.$$

The manner in which the specific gravity of a **permanent gas** was formerly obtained was by exhausting a thin glass globe by means of the air-pump and weighing it; then filling it with air at known temperature and pressure, and weighing; and lastly, pumping out the air, filling the globe with the gas at a similar temperature and pressure, and again weighing. After deducting the weight of the empty globe from each of the two latter weights, the weight of the gas was divided by that of the air.

Now, however, in modern laboratories all that is practically done away with, and the standard taken for the density of gases and vapours is hydrogen; because (1) it is the lightest known gas, and (2) we know the weight of any given volume of it without the necessity of weighing each time. Therefore, to take the density of a gas or vapour we weigh a given number of cubic centimetres of the gas, noting the temperature and pressure at the moment of weighing, and having corrected the volume so obtained to N.T.P., we divide this by the weight of the same number of c.c. of hydrogen. A litre of hydrogen at 0° C. and 760 mm. bar. weighs ·0896 gramme; therefore each c.c. of H will weigh ·0000896 gramme.

(*E*) Vapour Density.

After finding the percentage composition of substances by analysis, and from that calculating an empirical formula (which is done by dividing the percentage of each element by its own atomic weight, then, taking the lowest of these answers as unity, dividing all the others by it and expressing the mutual ratios in the simplest full numbers), it is necessary to prove whether the sum of such formula is the true molecular weight. Upon the theory that all molecules occupy a space double that of an atom of hydrogen, we can prove our case by taking the hydrogen density of the substance in vapour (if volatile), and then such vapour density × 2 = the true molecular weight. This research acts as a check upon our formula obtained by analysis, and may or may not lead to our having to multiply it until its sum equals the required weight thus found.

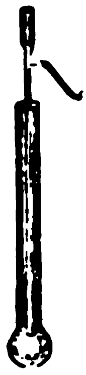

Fig. 24.

(*a*) **Meyer's Method.**—This is the simplest and most rapid process. The apparatus used is illustrated in fig. 24. The inner tube (A) is closed with a cork and arranged so that its bent delivery tube just dips under the surface of mercury contained in a trough. Any suitable liquid, boiling at a higher temperature than the body of which the density is to be taken, is placed in the outer tube (B), and heat being applied so as to boil the fluid, the air in the inner tube expands and passes off through the mercury. When bubbles of air cease to pass, some water is poured upon the surface of the mercury, and a graduated gas collecting tube, filled with water, is inverted over the delivery tube. A known weight of the substance, enclosed in a specially made minute stoppered bottle, is then introduced into the inner tube (A) by rapidly raising the cork, dropping the bottle in, and instantly closing. The vapour produced now displaces an equivalent volume of air, which passes into the measuring tube. When action ceases, the cork is opened to prevent back suction, and the air in the tube is measured, noting temperature and pressure. This volume in c.c. when corrected to N.T.P., and multiplied by ·0000896, gives the weight of a volume of hydrogen equal to that of the vapour, and lastly, by dividing the weight of the substance taken, by this calculated weight, we obtain the vapour density. The coefficient of expansion of all gases being practically equal, it is evidently the same thing whether we measure a volume of actual vapour at a given temperature, or that of an equivalent volume of air displaced by it at the same temperature. Such a minute quantity of the substance must be taken as shall not, when in vapour, more than displace the air contained in the inner tube of the apparatus (which should hold about 100 c.c.), otherwise the whole process manifestly fails. As the gas is collected over water it is necessary to refer to a table of the tension of aqueous vapour at the temperature of measuring, and to deduct it from the observed height of the barometer, before correcting to N.T.P.

(*b*) **Dumas' Process.**—A thin, clean, dry glass globe, about three inches in diameter, is employed. Its neck having been drawn out to a fine tube in the blowpipe flame, it is weighed, and the temperature and pressure noted. By gently heating the bulb and dipping the open end into the volatile liquid, a suitable quantity is drawn into the globe by the contraction of the air. Attaching a handle by means of wire, the sphere is plunged into an oil bath furnished with a thermometer, and is then heated somewhat above the volatilising point of the contained liquid. When all vapour has ceased to issue from the globe, the orifice is hermetically sealed, and the temperature and pressure again noted. The apparatus is allowed to cool, separated from the handle, cleansed, weighed, and the weight noted. The last step is to break off a fragment of the neck beneath the surface of a sufficiency of mercury, when, should the experiment have been carefully performed, the liquid enters the globe, completely filling it, and the capacity is ascertained by emptying its contents into a graduated glass measure. Supposing the experiment to have been perfectly successful, we have the following five data:—

1. Weight of globe filled with air.
2. Temperature and pressure at the time of weighing.
3. Weight of globe *plus* vapour.
4. Temperature and pressure at sealing.
5. Capacity of the globe.

Proceeding from these data, the first point is to find the actual weight of the globe. This is done by calculating the capacity of the globe from the temperature and pressure at the time of weighing to 0° C. and 760 mm. bar., and then multiplying the true volume thus found by ·001295, which is the weight of a cubic centimetre of air (1 litre at 0° C. and 760 mm. bar. = 1·295 gramme). Having thus obtained the weight of the air, it is deducted from the weight of globe and air, and the difference gives the true weight of the globe; and by deducting this latter from the weight of the globe *plus* vapour, we obtain the actual weight of the vapour. But as this weight is that of the volume of vapour at the temperature and pressure at the moment of sealing, it must be corrected to standard temperature and pressure, and the weight of an equal volume of hydrogen ascertained. To do this, the capacity of the globe is once more put down, and reduced from the temperature and pressure at sealing to 0° C. and 760 mm. bar., and the resulting volume is multiplied by ·0000896, which is the weight of 1 cubic centimetre of hydrogen. The product, which gives the actual weight of an equivalent volume of hydrogen, is then taken, and divided into the weight of the vapour already found, and the answer is the density.

(*F*) Note on Weights and Measures.

The American Pharmacopœia has entirely discontinued the use of any weights and measures except those of the metrical system, and the spelling of the terms has been Anglicised thus:—

gramme to *gram*, abbreviated to Gm.
litre to *liter* ,, ,, lit. or 1000 Cc.
cubic centimetre to *cubic centimeter*, abbreviated to Cc.

These abbreviations, being very convenient, will be employed in the following chapter on Volumetric Analysis, so that students may become accustomed to both systems of spelling and abbreviation.

CHAPTER VII.

VOLUMETRIC QUANTITATIVE ANALYSIS.

I. INTRODUCTORY REMARKS.

VOLUMETRIC analysis is that in which the quantity of any *reagent* required to perform a given reaction is ascertained, and the amount of the substance acted upon is found by calculation. The process of adding the reagent from a graduated measure is called **titration.**

(*A*) **Volumetric or standard solution** is a solution of definite strength, made by dissolving a given **weight** of a reagent **in grams** in a definite **volume** of water **in cubic centimeters.** Such solutions are usually made on the following principles :—

The theoretical **normal** solution is an imaginary one, containing 1 Gm. of hydrogen in 1 liter (1000 Cc.) of water, and a **normal** solution of any reagent is such a weight of the substance in Gm. (also 1 liter of water) as is capable of combining with, displacing, or otherwise performing a chemical function equal to that of 1 Gm. of hydrogen. This weight is termed the **equivalent** of the reagent, and it is ascertained as follows :—

(*a*) *The reagent is an element.* We divide the *atomic* weight of the element by its *valency*. Thus—

$$H' = 1, Cl' = 35·5, Br' = 80, I' = 127, O'' = 8, \text{etc.}$$

(*b*) *The reagent is an acid or an alkali.* We divide the molecular weight by the active combining power, as shown by the number of atoms of displaceable hydrogen in acids, and by the valency of the base in alkalies :—

Name.	Formula.	Equivalent.
Hydrogen	H	= 1
Hydrochloric acid . . .	HCl	= 36·37
Sulphuric acid	$H_2SO_4 \div 2$	= 48·91
Citric acid	$H_3C_6H_5O_7H_2O \div 3$	= 69·83
Sodium hydroxide . . .	$NaHO$	= 39·96
Calcium hydroxide . . .	$Ca(HO)_2 \div 2$	= 36·87
Potassium carbonate . . .	$K_2CO_3 \div 2$	= 68·95
Potassium bicarbonate . .	$KHCO_3$	= 99·88

(*c*) *The reaction is a special one, depending on a particular action.* We divide the molecular (or atomic) weight of the reagent by its combining power, as shown in the equation. For example, taking the case of the action between iodine and arsenious acid, we find the equation :—

$$As_2O_3 + 2I_2 + 2H_2O = As_2O_5 + 4HI.$$

Each atom of iodine being equivalent of one of hydrogen, it follows that each H would equal ¼ of As_2O_3 ; therefore a normal solution of that body would be 198 ÷ 4 = 49·5 Gm. per liter, and would exactly decolorize 1 atomic weight (= 127 Gm.) of iodine.

The following abbreviations are used to express the strength of standard solutions:—

N = a normal solution having 1 equivalent weight in Gm. per liter.
$\frac{N}{10}$ = a decinormal solution having $\frac{1}{10}$ equivalent weight in Gm. per liter.
$\frac{N}{100}$ = a centinormal " $\frac{1}{100}$ " " " "

(*B*) **An indicator** is a substance added to enable us to ascertain, by a change of color (or other equally marked effect), the exact point at which a given reaction is complete.

The principal indicators employed are prepared as follows:—

(1) Indicators for estimating acids or alkalies.

(*a*) *Litmus indicator.* Boil powdered litmus in alcohol of ·82 sp. gr. repeatedly till no more red color is extracted, and then digest the residue in an equal weight of cold distilled water. Pour or filter off, and then boil the blue powder remaining in 5 times its weight of distilled water; filter and preserve the filtrate in a bottle stoppered with a loose plug of cotton, so that air is admitted, but dust excluded. This indicator is blue with alkalies and red with acids, and is affected by all acids, including CO_2. It therefore does not give a reliable indication with alkaline carbonates unless the CO_2 is expelled by boiling.

(*b*) *Phenol-phthalein indicator.* Make a 1 per cent. solution of phenol-phthalein in diluted alcohol of ·937 sp. gr., *i.e.* 1 Gm. in 100 Cc. This solution is red with alkalies, and colorless with acids. It is not suitable as an indicator with ammonia or alkaline bicarbonates.

(*c*) *Rosolic acid indicator.* Dissolve 1 Gm. rosolic acid (or the commercial dyes known as *pæonin* or *aurin R*) in 10 Cc. diluted alcohol, and make up to 100 Cc. with distilled water. This solution gives a violet-red with alkalies, and a yellow with acids. It is specially useful in the estimation of alkaline ammonia salts.

(*d*) *Methyl-orange indicator.* Dissolve 1 Gm. of methyl orange (or the commercial dyes known as *helianthin*, *Poirrier's orange 3P* or *tropæolin D*) in 1000 Cc. of distilled water. Into this, carefully drop diluted sulphuric acid till the liquid turns red and just ceases to be transparent, and then filter. This solution is yellow with alkalies and red with mineral acids, but is not affected by CO_2 or boric acid, so that it is the best indicator for the analysis of alkaline carbonates and borax. It cannot, however, be used with oxalic acid or organic acids generally.

There are many other indicators, but the above are those really most generally useful in acidimetry or alkalimetry.

Note.—The U S.P. gives a very suitable warning as to the above indicators, which is worthy of being quoted in full. It says: "Each test-solution used as *indicator* should be examined as soon as prepared, and afterwards from time to time, as to its neutrality. If necessary, it should be brought, by the cautious addition of diluted sulphuric acid, or of a dilute solution of an alkali, to such a point that, when a few drops of it are added to 25 Cc. of water, a single drop of a centinormal acid or alkali, respectively, will distinctly develop the corresponding tints. Since many of the colored test-solutions are injured by exposure to light, it is best to preserve them in dark amber-colored vials."

(2) Indicators for special purposes.

(*a*) *Starch mucilage.* Mix 1 Gm. of starch (arrowroot is preferable) with 10 Cc. of cold water, and then add enough boiling water, with constant stirring, to make about 200 Cc. of a thin, transparent jelly. To preserve this solution for any length of time, 10 Gm. of zinc chloride should be added to it, and the solution transferred to small bottles, which should be well stoppered. It is used for the detection of free iodine, with which it strikes a dark blue.

(*b*) *Potassium chromate solution.* Dissolve 10 Gm. of pure K_2CrO_4 in 100 Cc. of water, then carefully drop in dilute solution of argentic nitrate till a slight red turbidity is produced, let settle, and pour off into a stoppered bottle. This solution gives a red precipitate with $AgNO_3$, but *not* until any chloride, bromide, iodide, or cyanide present has entirely combined with the silver.

(*c*) *Potassium ferricyanide solution.* Dissolve 1 part of potassium ferricyanide in about 10 parts of water. This solution must be made freshly when required, as it is rapidly decomposed by light. The freshly prepared aqueous solution, when mixed with some ferric chloride solution and diluted with water, must show a brown tint, free from turbidity or any shade of green.

(*C*) The apparatus specially employed in volumetric analysis.

1. *The measuring flask*, so constructed as to hold a definite amount of fluid (say 1000 or 100 Cc.) when filled up to the mark on the neck (fig. 25).

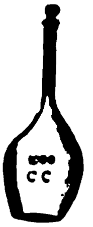

Fig. 25.

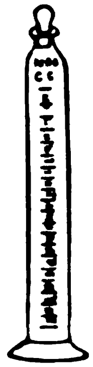

Fig. 26.

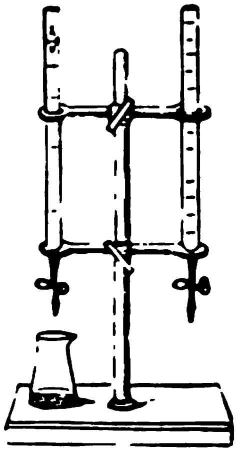
Fig. 27.

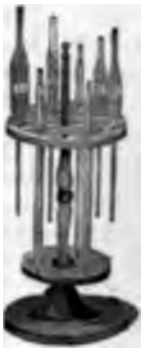
Fig. 28.

2. *The test mixer*, a cylindrical vessel, to hold 1 liter of fluid graduated in measures of 10 Cc. each (fig. 26).

3. *The burette*, a graduated tube, usually containing 100 Cc. and graduated in divisions of 1 Cc. (or 50 Cc. in $\frac{1}{10}$ Cc.), for containing and delivering the standard solution. This is fitted with a clamp or stopcock at the bottom, which, when pressed or turned, allows the contained liquid to run out at any regulated speed desired. It should also be furnished with an appliance called "Erdmann's float," which enables us to read the quantity of fluid delivered more accurately. (Fig. 27 shows two burettes in their stand as usually employed.)

4. *The pipette* is an instrument graduated to *deliver* a fixed volume of liquid (say 10, 20, 50, or 100 Cc.). Fig. 28 shows a set of such instruments arranged in a convenient stand.

(*D*) **Weighing operations.** The student should have a *tared* watch-glass for weighing out solids and a small stoppered bottle for weighing volatile liquids. By carefully keeping these much trouble is saved.

(1) *To weigh a solid.* Place the tared glass on the scale, and put on it what is judged to be a sufficient quantity of the article to be weighed, then weigh the whole and note the weight thus :—

Glass + substance	5·632 Gm.
Known tare of glass	5·132 ,,
Weight taken for analysis . . .	·500 ,,

(2) *To weigh a volatile liquid.* Fill the small stoppered bottle with the liquid and weigh ; pour out what is judged to be sufficient into the flask containing the indicator, replace the stopper and again weigh, noting each weight at the time thus :—

Total weight of bottle + fluid . . .	20·982 Gm.
Weight of bottle + fluid after pouring out	15·482 ,,
Weight of fluid taken	5·500 ,,

Note.—It is most important always to take the weights directly down in a note-book from the balance, and to cultivate the habit of *always replacing the weights in their proper holes in the weight box when finished.* This enables us to have a double check—(1) from the weights in the pans, and (2) from looking at the empty holes in the weight box. In weighing brass weights are used from 50 to 1 Gm. ; flat platinum weights from ·5 to ·01 Gm. ; and the rider on the beam is used for milligrams (*i.e.* ·009 to ·001). Before weighing, see that all the weights are in their right places in the box. At the conclusion of the weighing, read off the weights and put them down in a note-book, and then check that reading by putting them back into the box, looking, as you do so, at the note already made. Always close the case of the balance before using the rider, so as to prevent currents of air affecting the weight.

(*E*) **General modus operandi.** A known weight of the substance to be analyzed is accurately weighed, and, having been placed in a flask, and dissolved in, or diluted with, water (if necessary), the indicator is added, and the standard solution of the reagent is dropped in from a burette until the desired effect is produced. The number of Cc. of standard solution used having been noted, it is multiplied by the "*Cc. equivalent*" of the substance analyzed.

Suppose, for example, we desire to ascertain the purity of a sample of sodium hydroxide, and, having weighed out 1 Gm., we find that 24 Cc. of standard normal oxalic acid were required for exact neutralization. Normal oxalic acid is 62·85 Gm. per liter, or ·06285 in each Cc., and by the equation we find—

$$\underbrace{H_2C_2O_4 . 2H_2O}_{2)\underline{125\cdot7}} + \underbrace{2NaHO}_{2)\underline{79\cdot98}} = Na_2C_2O_4 + 4H_2O.$$

$$62\cdot85 \qquad 39\cdot90 = 39\cdot96 \text{ Gm. of NaHO, equivalent to } 62\cdot85 \text{ Gm. acid.}$$

The normal *liter equivalent* of NaHO is therefore 39·96, and the normal *Cc. equivalent* is 39·96 ÷ 1000 = ·03996 ; therefore each Cc. of acid used will represent ·03996 Gm. of soda. Then—

$$24 \times \cdot03996 = \cdot95904 \text{ Gm. of real NaHO in the 1 Gm. weighed out for analysis.}$$

Lastly—

$$\frac{\cdot95904 \times 100}{1} = 95\cdot904 \text{ per cent. real soda in sample.}$$

Expressing the above in rules to commit to memory, we have the following steps :—

I. Write out the equation and reduce the first side of it to normal equivalent weights.

II. According to the strength of the standard solution employed, divide the normal equivalent of the substance under analysis by 1000 (for normal solution), 10,000 (for decinormal), etc., thus getting the "**Cc. equivalent.**"

III. Multiply the number of Cc. of standard solution used from the burette by the *Cc. equivalent* of the substance analyzed, thus getting the actual amount of such substance in the quantity weighed out for analysis.

IV. If percentage be required, multiply the last result by 100, and divide by the weight taken for analysis.

(*F*) **The quantity of the substance to be weighed out for analysis.** Two considerations are to be kept in view, viz.: –

(*a*) The smaller the weight operated on, the greater will be the multiplication of any error in the final result.

(*b*) On the other hand, the weighing out of an amount of substance that will take more than one buretteful of the standard solution is to be deprecated as a source of error.

The point is to steer a judicious middle course, and this can always be done by considering the equation, reducing it to normal or decinormal, etc., equivalents, as the case may be, and then seeing how much will be required to take a reasonable number of Cc. of the standard solution, supposing the substance to be pure.

Thus taking the equation already considered,

$$\underbrace{H_2C_2O_4 . 2H_2O}_{\substack{2)125{\cdot}7\\ 62{\cdot}85}} + \underbrace{2NaHO}_{\substack{2)79{\cdot}92\\ 39{\cdot}96}} = Na_2C_2O_4 + 4H_2O,$$

it is evident that (roughly speaking) 40 Gm. of soda would take 1000 Cc. of normal acid, and *vice versâ*. If therefore we are using a 50 Cc. burette, we evidently must weigh out *somewhat less* than

$63 \div 20 = 3{\cdot}15$ oxalic acid
$40 \div 20 = 2{\cdot}00$ sodium hydrate

for titration by 50 Cc. of a normal solution.

In many cases the after-calculation may be altogether saved by weighing out a previously determined quantity, so that the number of Cc. of standard solution used will at once give the percentage. This idea is conveniently exemplified in the determination of iron in salts thereof. The normal equivalent of iron is (roughly speaking) 56, and the solutions employed in its estimation are usually decinormal, thus giving a liter equivalent of 5·6, and a Cc. equivalent of ·0056. If therefore we were to weigh out ·56 of iron, it is evident that each Cc. of a decinormal solution of a reagent for estimating it would represent $\frac{1}{100}$ of ·56 or 1 per cent. Similarly, if we take ·56 of any ferrous salt (containing one atom of iron in each molecule), each Cc. of the volumetric solution will represent 1 per cent. of iron present. Supposing the percentage of iron to be small (as in *Liq. ferri perchlor.*), we would take double the quantity or 1·12 Gm., and then each Cc. would equal ·5 per cent. of iron.

The rule may be thus stated for all titration: Calculate the Cc. equivalent of the substance you desire to estimate, taking into consideration the standard of the solution you are using (*i.e.* normal, decinormal, etc.), and, having multiplied by 100, weigh out this quantity for analysis. Then each Cc. of your solution used from the burette will = 1 per cent. of real substance in the quantity weighed out, and fractions of a Cc. = similar fractions of 1 per cent. When it is not desired to use a larger burette than 50 Cc., only 50 times the equivalent should be weighed, and then every ·5 Cc. = 1 per cent. With very accurate 10 Cc. burettes graduated in $\frac{1}{10}$ Cc. only 10 times the equivalent may be weighed, and then each $\frac{1}{10}$ Cc. = 1 per cent.; but, as before stated, the delicate work in this respect leads frequently to error.

(*G*) **Precautions in direct titration.** The standard solution may be added at first from the burette to the liquid analyzed at the rate of about ·5 Cc. at a time, and the liquid should be stirred or agitated after each addition. When it is seen, by the effect on the indicator, that the desired point is approaching, the standard solution should be added more carefully, and finally, at the rate of a single drop at one time, till the effect is obtained. The placing of a white porcelain slab, or a sheet of white paper, under the vessel containing the solution to be analyzed, helps us to see the changes in color more accurately. All titrations are better done in flasks, the contents of which can be readily agitated by holding the neck, and giving a circular movement from the wrist between each addition of the standard solution from the burette.

(*H*) **Residual titration.** This method is employed when the indication of the completion of a reaction is not easily seen. It consists in adding a definite excess of the reagent, and then, by means of another volumetric solution which gives a precise indication, ascertaining the amount of the reagent remaining uncombined. This residue, deducted from the total amount of original reagent added, will manifestly leave a difference due to the actual amount of that body taken up in performing the reaction. Supposing, for example, we are analyzing a body (W) by finding how many Ccs. of a volumetric solution (S) would be required to be added until no more precipitate forms, but that this exact point is difficult to see. We therefore choose another volumetric solution (S_2), that will exactly neutralize S in presence of an indicator giving a definite change of color when the reaction is complete. To W we add, say, 50 Cc. of S (taking care that this amount is more than sufficient to entirely precipitate W), and, having added our indicator, we titrate with S_2, of which we will suppose we used 10 Cc. Then

$50S - 10S_2 = 40$ Cc. S, required for the original precipitation.

And lastly—

40 × the "Cc. equivalent" of W = the weight of real article present in the amount thereof weighed out for analysis.

Having thus given a general idea of the mode of working, we now commence to practise with the chief standard solutions as follows.

II. STANDARD ACID SOLUTIONS (Alkalimetry).

The standard acids usually employed in volumetric analysis are thus prepared and used.

(*A*) Preparation.

(I.) *NORMAL OXALIC ACID.*

Strength:—$H_2C_2O_4 . 2H_2O$ = 125·7 ÷ 2 = 62·85 *Gm. per liter.*

(Usually rounded off as 63 Gm.)

This is made by powdering some *pure* oxalic acid, pressing it between the folds of blotting-paper (to remove any chance moisture), and weighing out exactly 62·85 Gm. in a tared beaker. The powder is then washed out with distilled water from the beaker into the liter measuring flask, which is nearly filled with water and slightly warmed to aid solution. When all is dissolved, more water is poured in till the solution arrives at the mark in the neck of the flask, and finally the whole is cooled down to 60° F., and is once more exactly made up to the line with water.

Note.—The acid used must leave no residue when heated to redness on platinum foil, and 1 Gm. must be entirely soluble in 14 Cc. of distilled water at 15° C. Should it not answer these tests it must be purified as follows:—Shake up 100 Gm. of the impure acid with 1 liter of water until saturated, and filter. Evaporate the filtrate down to 750 Cc., and let it cool and crystallize. Pour off from the deposit and again evaporate to crystallizing point, and set it to crystallize stirring occasionally to prevent the formation of large crystals. Finally drain the crystals, dry them on blotting-paper, and preserve in a well-stoppered bottle.

(II.) *DECINORMAL OXALIC ACID.*

Strength:—6·285 (6·3) *Gm. per liter.*

Take 100 Cc. of the normal acid, wash into a liter flask, and make up to the mark with distilled water.

(III.) *NORMAL SULPHURIC ACID.*

Strength:—H_2SO_4 = 97·82 ÷ 2 = 48·91 *Gm. per liter.*

(Usually rounded off to 49 Gm.)

Mix 30 Cc. ordinary strong sulphuric acid (98 per cent.) with 900 Cc. of distilled water, let it cool to 15° C., and then make up to 1050 Cc. This rough acid is then to be standardized as follows:—

(*a*) *With normal alkali.* Put 10 Cc. of the rough acid in a flask, add a few drops of phenol-phthalein, and run in normal solution of KHO or NaHO until a faint permanent pink is produced. Note the number of Cc. of normal alkali used, multiply by 100, and dilute 1000 Cc. of rough acid to this amount. Example 10 Cc. rough acid took 11·2 Cc. alkali; then 1000 Cc. acid are to be diluted to 1120 Cc., and 50 Cc. of this should exactly neutralize 50 Cc. of normal alkali.

(*b*) *With pure anhydrous sodium carbonate* (in the absence of reliable normal alkali). Weigh out 2·6463 (2·65) Gm. pure sodium carbonate, and dissolve in water in a flask; add a few drops of methyl orange, and run in the rough acid from a burette till the yellow changes to pink. Note the number of Cc. used, and then put 20 times this amount into the test mixer, and make up to 1 liter with water.

Note.—Pure Na_2CO_3 is best made by packing a percolator with good sodium bicarbonate, and percolating with distilled water until the fluid, passing through, gives no reaction with $AgNO_3$ or $BaCl_2$, after acidulating with HNO_3 and HCl respectively. The contents of the percolator are then dried and heated to redness, and the residue saved as "chemically pure Na_2CO_3 for standardizing acids."

(IV.) *DECINORMAL SULPHURIC ACID.*

Strength.—4·891 (4·9) *Gm. per liter.*

Put 100 Cc. normal sulphuric acid into a liter flask, and make it up to the mark with distilled water.

(V.) *NORMAL HYDROCHLORIC ACID.*

Strength: HCl = 36·37 *Gm. per liter.*

(Usually rounded off to 36·5 Gm.)

Make up 130 Cc. of ordinary 32 per cent. acid to 1 liter with distilled water. This makes a rough acid rather too strong, which is standardized as follows:—

(*a*) *With normal alkali.* Put 10 Cc. rough acid into a flask, and titrate with normal alkali as above directed for sulphuric acid. Note number of Cc. alkali used, multiply by 100, and make 1000 Cc. of acid of equal strength. Supposing 10 Cc. rough acid took 11 Cc. normal alkali, then—

$$\frac{1000 \times 10}{11} = 909{\cdot}1 \text{ Cc. rough acid to be made to 1 liter.}$$

50 Cc. of this acid should then exactly neutralize 50 Cc. of normal alkali.

(*b*) *With crystallised calcium carbonate* (in the absence of reliable normal alkali).

$$\underbrace{CaCO_3}_{\substack{2)99{\cdot}76 \\ 49{\cdot}88}} + \underbrace{2HCl}_{\substack{2)72{\cdot}74 \\ 36{\cdot}37}} = CaCl_2 + CO_2 + H_2O.$$

Therefore 1 liter of normal acid should dissolve 49·88 Gm. of $CaCO_3$, and 50 Cc. would therefore dissolve 2·494 Gm. (or rounded off to 2·5).

Weigh out 3 Gm. of broken (but not powdered) *calc-spar* in a small tared beaker, and run on 50 Cc. of rough acid. When all action has ceased, pour off, wash by decantation with cold water, and then pour off, close, and dry the beaker and contents by spontaneous evaporation in a warm place. Weigh and deduct from original weight; difference equals $CaCO_3$ dissolved. Supposing that this difference be 2·75, then :—

$$2{\cdot}75 - 2{\cdot}5 = {\cdot}25;$$

therefore the acid was $\frac{1}{10}$ too strong, and requires diluting accordingly.

(VI.) *DECINORMAL HYDROCHLORIC ACID.*

Strength:—3·637 (3·65) *Gm. per liter.*

Dilute 10 Cc. normal acid to 100 Cc. with distilled water.

(*B*) **Estimation of Alkaline Hydroxides and Borax.**

Any of the standard acids may be used for this purpose, but, if normal acid be employed, sulphuric is preferable, especially in winter, because normal oxalic tends to crystallize in cold weather. A proper weight of the alkali having been taken and dissolved, or if in solution diluted, a few drops of solution of phenol-phthalein are added, and the acid is run in from the burette until the red color is just discharged. The addition of the acid is made at the rate of about ½ Cc. at a time (with constant agitation after each addition) until the color shows signs of lightening, then the acid is added in $\frac{1}{10}$ of a Cc. until the color disappears. With ammonia rosolic acid is used as indicator, and the acid added until the red turns yellow. For borax use methyl orange.

The following table shows the convenient quantities to weigh, the indicator to use, and the equivalent weight of the substance for each Cc. of normal acid used :—

Name and formula.	Gm. to weigh.	Indicator.	Accurate equivalent.	Approximate equivalent.
Strong ammonia solution NH_3	1·7	rosolic acid	·01701	·017
Dilute " " NH_3	3·4	" "	·01701	·017
Solution of potash KHO	28·0	phenol-phthalein	·05599	·056
" " soda $NaHO$	20·0	"	·03996	·040
Potassium hydroxide KHO	0·56	"	·05599	·056
Sodium " $NaHO$	0·40	"	·03996	·040
Spirit of ammonia NH_3	3·40	rosolic acid	·01701	·017
Borax $Na_2B_4O_7 . 10H_2O$	1·91	litmus	·19046	·191

The following are typical equations of the chief reactions :—

(*a*) *Liquor ammoniæ fort. and liquor ammoniæ.*

$$H_2SO_4 + 2NH_3 . H_2O = (NH_4)_2SO_4 + 2H_2O.$$

(*b*) *Potassium hydroxide or sodium hydroxide* or their *solutions.*

$$H_2SO_4 + 2NaHO = Na_2SO_4 + 2H_2O.$$
$$H_2SO_4 + 2KHO = K_2SO_4 + 2H_2O.$$

(*c*) *Metallic sodium* (thrown on water, and the resulting solution of NaHO titrated with phenol-phthalein as indicator).

$$Na_2 + 2H_2O = 2NaHO + H_2.$$
$$H_2SO_4 + 2NaHO = Na_2SO_4 + 2H_2O.$$
$$\text{Therefore } H_2SO_4 = Na_2.$$

(*d*) *Borax* (with methyl orange).

$$H_2SO_4 + Na_2B_4O_7 . 10H_2O = Na_2SO_4 + H_2B_4O_7 + 10H_2O.$$

(*C*) Estimation of Alkaline Carbonates.

By titration with normal sulphuric acid, with methyl orange as the indicator, because the CO_2 given off does not affect this indicator. The acid is added till the color just changes from yellow to pink. The change is better seen when a very small quantity of the methyl orange is used, just sufficient to tinge the liquid pale yellow. For ammonium carbonate use rosolic acid.

Note.—Alkaline carbonates may also be titrated with standard oxalic acid and litmus indicator, provided the process is conducted in a boiling solution so as to drive off the CO_2 evolved, but no practical analyst now thinks of using this method when standard sulphuric acid is available.

The following table shows the convenient quantities to weigh, the indicator to be used, and the equivalent of the substance for each Cc. of normal acid expended:—

Name and formula.	Gm. to weigh.	Indicator.	Accurate equivalent.	Approximate equivalent.
Official carbonate of ammonia $N_3H_{11}C_2O_5$	2·613	rosolic acid	·05226	·053
Lithium carbonate Li_2CO_3	·500	methyl orange	·036935	·037
Potassium bicarbonate $KHCO_3$	1·000	„	·09988	·100
Potassium carbonate K_2CO_3	0·69	„	·068955	·069
Sodium bicarbonate $NaHCO_3$	0·85	„	·08385	·084
Sodium carbonate (anhydrous)	1·000	„	·052925	·053

The following are typical equations for the chief reactions involved:—

(*a*) *Crystallized sodium carbonate.*

$$H_2SO_4 + Na_2CO_3 . 10H_2O = Na_2SO_4 + CO_2 + 11H_2O.$$

(*b*) *Dried sodium carbonate.*

Similar equation without the H_2O on each side.

(*c*) *Sodium bicarbonate.*

$$H_2SO_4 + 2NaHCO_3 = Na_2SO_4 + 2CO_2 + 2H_2O.$$

(*d*) *Potassium carbonate.*

$$H_2SO_4 + K_2CO_3 = K_2SO_4 + CO_2 + 2H_2O.$$

(*e*) *Potassium bicarbonate.*

$$H_2SO_4 + 2KHCO_3 = K_2SO_4 + 2CO_2 + 2H_2O.$$

(*f*) *Commercial "carbonate of ammonia.*

$$3H_2SO_4 + 2(N_3H_{11}C_2O_5) = 3(NH_4)_2SO_4 + 4CO_2 + 2H_2O.$$

(*D*) Estimation of Organic Salts of the Alkalies.

Organic salts of potassium, sodium, or lithium are examined by weighing out the salt in a platinum or porcelain crucible, and then heating to redness in contact with the air until all is perfectly charred. The crucible is now cooled, and its contents dissolved in boiling water and filtered into a flask, and the filter washed with boiling water until the washings do not affect red litmus paper. The contents of the flask are then colored by methyl orange and titrated with standard sulphuric acid, in the manner described above for alkaline carbonates. The ignition causes the conversion of the organic salt into an alkaline carbonate.

The following table shows the best quantities to weigh out, and the equivalent weight of the substance for each Cc. of normal acid used:—

Name and formula.	Gm. to weigh.	Accurate equivalent.	Approximate equivalent.
Lithium benzoate $LiC_7H_5O_2$	1·000	·12772	·128
„ citrate $Li_3C_6H_5O_7$	1·000	·0698566	·07
„ salicylate $LiC_7H_5O_3$	1·000	·14368	·144
Potassium acetate $KC_2H_3O_2$	1·000	·09789	·098
„ bitartrate $KHC_4H_4O_6$	1·880	·18767	·188
„ citrate $K_3C_6H_5O_7$	1·080	·10786	·108
„ sodium tartrate $KNaC_4H_4O_6 . 4H_2O$.	1·410	·14075	·141
Sodium acetate $NaC_2H_3O_2 . 3H_2O$	1·360	·13574	·136
„ benzoate $NaC_7H_5O_2$	2·000	·14371	·144
Strontium lactate $Sr(C_3H_5O_3)_2$	1·330	·13244	·133

The following are specimens of typical equations for some of the above reactions, on the model of which the rest can easily be constructed :—

(*a*) *Lithium benzoate.*

$2LiC_7H_5O_2 + 6O_2 = Li_2CO_3 + 4CO_2 + 5H_2O$;
then $Li_2CO_3 + H_2SO_4 = Li_2SO_4 + CO_2 + H_2O$;
therefore $H_2SO_4 = 2LiC_7H_5O_2$.

(*b*) *Cream of tartar.*

$2KHC_4H_4O_6 + 5O_2 = K_2CO_3 + 7CO_2 + 5H_2O$;
then $K_2CO_3 + H_2SO_4 = K_2SO_4 + CO_2 + H_2O$;
therefore $H_2SO_4 = 2KHC_4H_4O_6$.

(*c*) *Neutral potassium tartrate.*

$2(K_2C_4H_4O_6 . H_2O) + 5O_2 = 2K_2CO_3 + 6CO_2 + 6H_2O$;
then $2H_2SO_4 + 2K_2CO_3 = 2K_2SO_4 + 2CO_2 + 2H_2O$;
therefore $2H_2SO_4 = 2K_2C_4H_4O_6 . H_2O$.

(*d*) *Rochelle salt.*

$2(KNaC_4H_4O_6 . 4H_2O) + 5O_2 = 2KNaCO_3 + 6CO_2 + 12H_2O$;
then $2KNaCO_3 + 2H_2SO_4 = 2KNaSO_4 + 2CO_2 + 2H_2O$;
therefore $2H_2SO_4 = 2KNaC_4H_4O_6 . 4H_2O$.

(*e*) *Potassium citrate.*

$2K_3C_6H_5O_7 + 9O_2 = 3K_2CO_3 + 9CO_2 + 5H_2O$;
then $3K_2CO_3 + 3H_2SO_4 = 3K_2SO_4 + 3CO_2 + 3H_2O$;
therefore $3H_2SO_4 = 2K_3C_6H_5O_7$.

(*E*) Estimation of Lead Salts.

(*a*) *Plumbic acetate.*

Weigh 3 Gm., dissolve in plenty of water (the flask ⅓ full), with a drop or two of acetic acid to clarify, and then carefully drop in normal sulphuric acid till precipitation ceases.

Take 3 Gm., and use the following equation :—

$$H_2SO_4 + Pb(C_2H_3O_2)_2 . 3H_2O = PbSO_4 + 2HC_2H_3O_2 + 3H_2O.$$

(*b*) *Liquor plumbi subacetatis.*

Take 13·63 Gm., add methyl orange, titrate with normal sulphuric acid, and apply the equation :—

$$2H_2SO_4 + Pb_2O(C_2H_3O_2)_2 = 2PbSO_4 + 2HC_2H_3O_2 + H_2O.$$

III. STANDARD ALKALI SOLUTION.

NORMAL ALKALI.

Strength:—39·96 (40) *Gm.* *NaHO or* 55·99 (56) *Gm.* *KHO in* 1000 *Cc.*

(*A*) Preparation and Check.

As the commercial alkalies are not pure, this solution has to be made as follows: -

Dissolve 54 Gm. of ordinary caustic soda or 75 Gm. of caustic potash in 900 Cc. of distilled water, and let it cool to 15° C. (59° F.), and make up to 1050 Cc. Now place 20 Cc. of normal acid in a flask, add phenol-phthalein, and run in some of this crude alkali from a burette until a faint pink is produced. Note the number of Cc. of alkali used, put 50 times that volume of the crude alkali solution into a test mixer, and make up to the 1000 Cc. mark with distilled water. On again checking, 20 Cc. of the acid should take exactly 20 Cc. of the perfected alkali for exact neutralization. When accurate normal acid is not available, weigh out ·6285 (·63) Gm. *pure* oxalic acid, dissolve in 10 Cc. of water (in a 100 Cc. flask), add phenol-phthalein, and titrate with the crude alkali. Note the number of Cc. of crude alkali used, multiply by 100, and then put that number of Cc. of crude alkali into a liter flask, and make up to 1000 Cc. at 15° C. (59° F.). This latter method is preferred by the U.S.P., which also considers KHO solution to be more serviceable than NaHO, as having a less action on glass vessels. Should any less volume of normal alkali than 1000 Cc. be desired, multiply the Cc. required by the number of Cc. of crude alkali used, divide by 10, and the answer will be the Ccs. of crude alkali to be made up to the desired volume.

Normal alkali diluted from 100 Cc. to 1000 Cc. gives decinormal, and from 10 Cc. to 1000 Cc. yields centinormal, alkali.

Standard alkali should be kept in bottles fitted with a rubber cork, through which passes a tube filled with soda-lime to prevent the entrance of CO_2 from the air.

(*B*) Acidimetry.

Standard alkali is used for taking the strength of acids by simply weighing out a quantity of the acid, and then running in the soda in presence of phenol-phthalein, with the precaution already described on page 111. The following are some of the more important equations:—

(*a*) $NaHO + HCl = NaCl + H_2O$
(*b*) $NaHO + HNO_3 = NaNO_3 = H_2O$
(*c*) $NaHO + HC_2H_3O_2 = NaC_2H_3O_2 + H_2O$.
(*d*) $2NaHO + H_2SO_4 = Na_2SO_4 + 2H_2O$.
(*e*) $2NaHO + H_2C_4H_4O_6 = Na_2C_4H_4O_6 + 2H_2O$.
(*f*) $3NaHO + H_3C_6H_5O_7 . H_2O = Na_3C_6H_5O_7 + 4H_2O$.

The following table shows the convenient amount of each acid to weigh out, and the equivalent weight of real acid for each Cc. of normal alkali used:—

Name and formula.	Gm to weigh.	Accurate equivalent	Approximate equivalent.
Acetic $HC_2H_3O_2$	6·0	·05986	·060
Citric $H_3C_6H_5O_7 . H_2O$	3·5	·06983	·070
Hydrobromic HBr	8·08	·08076	·081
Hydrochloric HCl	3·64	·03637	·0365
Hypophosphorous $H . PH_2O_2$	6·6	·06598	·066
Lactic $HC_3H_5O_3$	4·5	·08979	·090
Nitric HNO_3	3·145	·06289	·063
Oxalic $H_2C_2O_4 . 2H_2O$	3·15	·06285	·063
Sulphuric H_2SO_4	4·9	·04901	·049
Tartaric $H_2C_4H_4O_6$	3·75	·07482	·075

In cases of dilute acids 10 times the above weight may as a rule be taken.

The acidimetry of phosphoric acid is dependent on the indicator employed. If we use phenol-phthalein, we complete the formation of the dibasic phosphate at the change of color thus:—

$$(a)\ H_3PO_4 + 2KHO = K_2HPO_4 + 2H_2O;$$

while with methyl orange the completion of the formation of the monobasic phosphate is indicated at the change thus:—

$$(b)\ H_3PO_4 + KHO = KH_2PO_4 + H_2O;$$

therefore the equivalents are:—

Name and formula.	Indicator.	Accurate equivalent.	Approximate equivalent.
Phosphoric H_3PO_4	phenol-phthalein	·0489	·049
„ „	methyl orange	·0978	·098

(*C*) Checking the Strength of Chloral Hydrate.

This method (used in America) is thus applied: 2 Gm. of chloral hydrate are dissolved in 10 Cc. of water; this solution is tested for acidity by litmus paper, and if acid it is *exactly neutralized* by a few drops of *very* weak soda. 20 Cc. of standard alkali are then added, and the whole is allowed to stand for half an hour to complete the decomposition into chloroform and sodium formate. Phenol-phthalein having been added, standard acid is run in from a burette till the color changes, and the number of Cc. of acid used having been deducted from 20, the difference gives the Cc. of alkali used up by the chloral. Then on the equation

$$2C_2HCl_3O\,.\,H_2O + 2NaHO = 2CHCl_3 + 2NaCHO_2 + 2H_2O$$

each Cc. of alkali so used represents ·1655 Gm. of chloral hydrate.

IV. STANDARD SOLUTION OF ARGENTIC NITRATE.

Strength:—*Decinormal* $\frac{N}{10}$ = 16·955 (17) *Gm. per* 1000 *Cc.*

(*A*) Preparation.

Dissolve 16·955 Gm. pure $AgNO_3$ in distilled water, and make up to 1 liter (1000 Cc.). The solution should be kept in dark amber-colored stoppered bottles, and carefully protected from dust.

Check. As argentic nitrate is not always pure, the solution when thus made should be standardized by weighing out ·1 (1 Decigm.) of *pure* powdered sodium chloride, dissolving it in water in a small beaker, adding sufficient potassium chromate indicator to color it yellow, and then running in the silver solution, with constant stirring, until the last drop just causes the color to change from yellow to pink. This should take 17 Cc. of silver solution, because—

$$\underbrace{AgNO_3}_{10)169{\cdot}55} + \underbrace{NaCl}_{10)58{\cdot}37} = AgCl + NaNO_3,$$

16·955 5·837 = Gm. of NaCl, equivalent to 1000 Cc. $\frac{N}{10}$ $AgNO_3$,
and ·005837 × 17 = ·099429 (practically ·1 Gm.).

If the silver solution be too strong, it should be diluted by the rules already given (see *ante*); but if too weak, it must have more $AgNO_3$ added, and then again checked and diluted.

Preparation of pure sodium chloride. Make a saturated solution of the best commercial salt, and pass in dry hydrochloric acid gas till precipitation ceases. Separate the crystalline precipitate, and dry at a temperature below redness, but sufficiently high to expel all traces of free acid.

(*B*) Estimation of Halogens in Soluble and Neutral Salts.

Decinormal silver solution is used for the estimation of haloid salts by weighing out any quantity ranging between ·2 and ·5 (2 or 5 Decigm.), dissolving and titrating, K_2CrO_4 being used as the indicator, exactly as above described. This process is only accurate in a perfectly neutral solution. If the solution be acid, then the estimation must be done by residual titration with KCNS (see p. 118). The following are some typical equations:—

(*a*) *Potassium bromide.*

$$AgNO_3 + KBr = AgBr + KNO_3.$$

(*b*) *Ammonium bromide.*

$$AgNO_3 + NH_4Br = AgBr + NH_4NO_3.$$

(*c*) *Potassium iodide.*

$$KI + AgNO_3 = AgI + KNO_3.$$

Note.—Bromides, if adulterated with iodides, will take *less* silver than they ought, but if the impurity be chloride, they will take *more*. Therefore they must neither take less nor *more* than the correct amount.

The principle on which an excess of silver used can be calculated to percentage of KCl present in any sample of KBr is best explained by an example.

·238 Gm. of impure KBr was found to take 21 Cc. of $\frac{N}{10}$ $AgNO_3$: what percentage of KBr did it contain?

·238 KBr would require 20 Cc. $\frac{N}{10}$ $AgNO_3$.
·238 KCl ,, ,, $\underline{31·94\text{ Cc.}}$ $\frac{N}{10}$ $AgNO_3$.

Theoretical difference 11·94 due to KCl;
but in this case the practical difference was 31·94 − 21 = 10·94.

Therefore—

$$\frac{10·94 \times 100}{11·94} = 91·63 \text{ per cent. of KBr, leaving } 8·37 \text{ KCl,}$$

or 21 − 20 = 1, and

$$\frac{1 \times 100}{11·94} = 8·37 \text{ per cent. of KCl and } 91·63 \text{ KBr,}$$

which is as nearly correct as can be obtained arithmetically.

The following table shows the salts thus estimated, with the convenient quantities to weigh out and weight of each salt equivalent to 1 Cc. of decinormal silver nitrate:—

Name and formula.	Gm. to weigh.	Accurate equivalent.	Approximate equivalent.
Ammonium bromide NH_4Cl	·30	·009777	·00980
,, chloride NH_4Cl	·20	·005338	·00535
Calcium bromide $CaBr_2$	·25	·009972	·01
Lithium bromide LiBr	·30	·008677	·0087
Potassium bromide KBr	·50	·011879	·0119
,, chloride KCl	·30	·00744	·0745
,, iodide KI	·50	·016556	·0166
Sodium bromide NaBr	·30	·010276	·0103
,, chloride NaCl	195	·005837	·00585
,, iodide NaI	·50	·014953	·015
Strontium bromide $SrBr_2$	·30	·012341	·0123
,, iodide SrI_2	·30	·017018	·01702
Zinc bromide $ZnBr_2$	·30	·011231	·01125
,, chloride $ZnCl_2$	·30	·006792	·0068
,, iodide ZnI_2	·30	·015908	·01591

(*C*) Estimation of Hydrocyanic Acid.

Silver solution is also used for taking the strength of hydrocyanic acid, which may be done by two methods as follows:—

(A) *Half precipitation process* (B.P.). Weigh 5·4 Gm., add a drop of solution of litmus, and then a few drops of NaHO so as to cause strong alkalinity. Now carefully drop in the silver solution from the burette, with constant agitation, until a *faint permanent cloud* of AgCN is produced. If, during the operation, the litmus becomes red, more NaHO must be added to keep it blue. The following equations explain the reaction, when it is remembered that the double cyanide of silver and sodium formed in equation (*b*) is soluble in water, while the AgCN produced in (*c*) is insoluble; therefore the formation of the slightest trace of a permanent precipitate indicates the completion of reaction (*b*) when exactly ½ the total CN is in combination with the silver :—

$$\begin{aligned}
&(a)\ 2HCN + 2NaHO = 2NaCN + 2H_2O.\\
&(b)\ 2NaCN + AgNO_3 = AgCN . NaCN + NaNO_3.\\
&(c)\ AgCN . NaCN + AgNO_3 = 2AgCN + NaNO_3.
\end{aligned}$$

Therefore— $2HCN = AgNO_3$.

So that 1000 Cc. $\frac{N}{10}$ $AgNO_3$ are equivalent to 5·4 Gm. of HCN.

Potassium cyanide is done in the same way, using about ·6 Gm., and $AgNO_3 = 2KCN$.

(B) *Complete precipitation process* (U.S.P.). Mix in a 100 Cc. flask ·27 Gm. of hydrocyanic acid with sufficient water and MgO to make an opaque mixture of about 10 Cc. Add 2 or 3 drops of solution of potassium chromate, and titrate as directed for haloid salts. The equation being

$$HCN + AgNO_3 = AgCN + HNO_3,$$

each Cc. of silver used will represent ·002698 HCN (or practically ·0027); and seeing that ·27 was taken, each Cc. will equal 1 per cent. This process is applied to crude *acidum hydrocyanicum*, which is then diluted till it shows exactly 2 per cent. real HCN. In ordinary cases more substance should be taken for analysis, preferably from 1·35 Gm. up to 5·4 Gm. With correct 2 per cent. HCN, 1·35 Gm. takes 10 Cc. silver solution. The object of the MgO is to remove the free HNO_3 as soon as formed.

The following table shows convenient amounts to weigh, and the equivalent weights for 1 Cc. of $\frac{N}{10}$ silver nitrate : —

Name and formula.	Gm. to weigh.	Accurate equivalent.	Approximate equivalent.
Hydrocyanic acid (with chromate) HCN	1·35	·002698	·0027
,, ,, (with NaHO) HCN	1·35	·005396	·0054
Potassium cyanide (with NaHO) KCN	·65	·013002	·013

V. STANDARD SOLUTION OF SODIUM CHLORIDE.

Strength :—Decinormal $\frac{N}{10}$ = 5·837 (5·84) *Gm. per* 1000 *Cc.*

(*A*) Preparation.

Dissolve 5·837 Gm. *pure* NaCl in 900 Cc. of water, and when brought exactly to 15° C. make up 1000 Cc. Each Cc. = ·005837 Gm. real NaCl. Pure sodium chloride is made as above described (p. 115), or perfectly colorless and transparent crystals of rock salt may be employed.

(*B*) Uses.

For the estimation of silver in solutions of its salts, the titration being continued (with good stirring occasionally) until the last drop causes no further precipitate of AgCl. Insoluble salts, such as Ag_2O, are dissolved in a sufficiency of dilute nitric acid, avoiding any great excess. Decinormal NaCl can also be employed to check the strength of decinormal $AgNO_3$ solution (which it should exactly equal Cc. to Cc.), as more convenient than weighing out NaCl every time. The following table gives the equivalent for each Cc. of decinormal NaCl:—

Name and formula.	Gm. to weigh.	Accurate equivalent.	Approximate equivalent.
Silver Ag	·27	·010766	·0108
Argentic nitrate $AgNO_3$	·34	·016955	·017
,, oxide Ag_2O	·232	·011564	·0116
Argenti nitras dilutus	1·00	·016955	·017

When the silver solution is neutral, it is often more accurate to add a known volume of decinormal NaCl, more than sufficient to precipitate all the silver, and then having added potassium chromate as indicator, to proceed by residual titration with decinormal $AgNO_3$. The U.S.P. applies this method to both *diluted* and *fused* silver nitrate, but it does the ordinary crystallized nitrate by direct titration as above explained.

VI. STANDARD SOLUTION OF POTASSIUM THIOCYANATE (SULPHOCYANIDE).

Strength:—Decinormal $\frac{N}{10}$ = 9·699 (9·7) *Gm. per* 1000 *Cc.*

(*A*) Preparation and Check.

Dissolve 10 Gm. of potassium thiocyanate (sulphocyanide) in 1000 Cc. of water. This solution is a little too strong, and must then be standardized as follows:—Take in a flask 10 Cc. of decinormal silver nitrate, acidulate with 5 Cc. of diluted nitric acid (1 in 7), and then add as indicator ½ Cc. of a solution of ferric ammonium sulphate (10 per cent. strength). Now titrate with the crude thiocyanate solution by shaking constantly until a slight permanent reddish tint is produced. The thiocyanate will first precipitate the silver as thiocyanate, and, when that is finished, will strike the well-known reddish color of ferric thiocyanate with the indicator. The red is always produced when the solution is dropped in, but it disappears on shaking so long as any silver remains unprecipitated. Note the number of Cc. of crude thiocyanate used, and make every 10 Cc. of that solution up to this number. Thus supposing that 10 Cc. decinormal silver nitrate took 10·5 Cc. crude sulphocyanate, and we had 980 Cc. left to make correct, then—

$$\frac{10·5 \times 980}{10} = 1029 \text{ Cc.}$$

So that 980 Cc. made up with distilled water to 1029 Cc. will give true decinormal thiocyanate, of which 50 Cc. should exactly balance 50 Cc. decinormal silver nitrate when tried again in a similar manner. Each Cc. of the perfected solution will then contain ·009699 (·0097) KCNS.

(*B*) Estimation of Silver in Acid Solutions.

This is done exactly as above described, and may be usefully applied to any compound of silver soluble in nitric acid. The equivalents for each Cc. are ·010766 (·0108) Ag and ·016955 (·017) $AgNO_3$.

(*C*) Estimation of Haloid Salts in Acid Solutions.

This is an application of residual titration, known as Volhard's method, and is, in certain cases, a much better idea for the estimation of haloid salts than the direct method with the chromate indicator, because it may be used in the presence of nitric acid, thus enabling a chloride, bromide, or iodide to be estimated in presence of a phosphate or other salt which precipitates silver in a neutral solution. It depends upon entirely precipitating the chloride in the presence of nitric acid by a known volume of decinormal silver nitrate, and then estimating the excess thereof, left uncombined with the chloride, by standard solution of ammonium thiocyanate (sulphocyanate), using solution of ferric ammonium sulphate for the indicator as above described. The U.S.P. applies it to the estimation of the iodide in *ferri iodidum saccharatum* and in *syr. ferri iodidi.* Of both these it takes 1·55 Gm., dissolves in, or dilutes with, 20 or 10 Cc. of water respectively, and then adds 22 Cc. or 11 Cc. respectively of decinormal silver nitrate. To this 5 Cc. of diluted nitric acid and ½ Cc. of ferric ammonium sulphate solution having been added, the whole is titrated with decinormal KCNS as already described, and not more than 2 Cc. or 1 Cc. respectively should be required. Taking the case of the syrup, we have—

Decinormal silver added . . . 11 Cc.
,, sulphocyanate taken . 1 Cc.
Difference . . . 10 Cc., due to the silver precipitated as iodide.

Then 10 × ·015477 (·0155) = ·155 real FeI_2 present, or 10 per cent. of the 1·55 syrup started with. Ferrous bromide and chloride may be similarly estimated:—

Name and formula.	Accurate equivalent.	Approximate equivalent.
Ferrous bromide $FeBr_2$	·01077	·0108
,, chloride $FeCl_2$	·006331	·00635

VII. STANDARD SOLUTION OF IODINE.

Strength:—*Decinormal* $\frac{N}{10}$ = 12·635 (12·7) *Gm. per* 1000 *Cc.*

(*A*) Preparation and Check.

Weigh out 12·635 (12·7) Gm. of pure iodine, and place it in a liter flask with 18 Gm. of potassium iodide and about 200 Cc. of water, agitate till dissolved, make up to 1000 Cc. with water, and preserve in small stoppered bottles in a dark place. Each Cc. = ·012635 (·0127) I.

Preparation of pure iodine. Heat powdered iodine in a flat porcelain dish on a boiling-water bath, with constant stirring, for 20 minutes. Rub it up in a glass mortar with 5 per cent. of its weight of pure potassium iodide, and return to the dish. Place a clean, dry funnel over the dish and heat on a sand bath, when the pure iodine will sublime and collect on the funnel, from which it is detached, and kept in a well-stoppered bottle.

Check. To standardize the strength of the solution (if desired), test it against ·2 Gm. (2 Decigm.) of pure As_2O_3 as hereafter described.

(*B*) Estimation of Arsenious Acid.

For *arsenious acid,* weigh out 1 Decigm. of the As_2O_3, and dissolve it in boiling water by the aid of ten times its weight of $NaHCO_3$. Let it cool, add some mucilage of starch, and titrate with the iodine solution until a faint permanent blue color is obtained. Then apply the equation:—

$$2I_2 + As_2O_3 + 5H_2O = 2H_3AsO_4 + 4HI.$$

Each Cc. of $\frac{N}{10}$ iodine used = ·004942 (·00495) As_2O_3.

For *liquor acidi arseniosi* or *liquor potassii arsenitis* use 24·7 Cc. and 2 Gm. $NaHCO_3$.

(*C*) Estimation of Sulphurous Acid and Sulphites.

For *sulphurous acid* weigh out 2 Gm. from a stoppered bottle, and dilute it with 25 Cc. of water. Add starch mucilage, and run in the iodine solution until the faintest possible *permanent* blue appears. Then apply the equation:—

$$I_2 + H_2O + SO_2 . H_2O = H_2SO_4 + 2HI;$$

whereby each Cc. $\frac{N}{10}$ iodine used = ·003195 (·032) SO_2.

For *sulphites* dissolve in 25 Cc. of water and proceed as above.

The following table shows the convenient amounts to weigh, and the equivalent for 1 Cc. $\frac{N}{10}$ iodine of the salts named:—

Name and formula.	Gm. to weigh.	Accurate equivalent.	Approximate equivalent.
Potassium sulphite $K_2SO_3 . 2H_2O$	·485	·009692	·0097
Sodium bisulphite $NaHSO_3$	·26	·005193	·0052
,, sulphite $Na_2SO_3 . 7H_2O$	·63	·012579	·0126
Sulphurous acid H_2SO_3	2·00	·004093	·0041
Sulphur dioxide (in sulphurous acid) SO_2	2·00	·003195	·0032

(*D*) Estimation of Antimony Potassium Tartrate.

This salt absorbs iodine on a similar principle of indirect oxidation to that already shown for As_2O_3. The reaction may be thus expressed:—

$$KSbOC_4H_4O_6 . H_2O + I_2 + 4NaHCO_3 + H_2O = KNaC_4H_4O_6 + 2NaI + NaSbO_3 + 4CO_2 + 4H_2O.$$

Therefore each atom of iodine can oxidize ½ of the molecular weight of the tartrate. In practise ·331 Gm. of the salt is dissolved in 10 Cc. of water, and to this 20 Cc. of cold saturated solution of sodium bicarbonate is added, together with a little starch mucilage, and the whole is titrated with $\frac{N}{10}$ iodine till a faint permanent blue is produced. The number of Cc. of iodine used multiplied by ·01656 (·0166) gives the amount of real tartrate present, which should be 100 per cent. The $NaHCO_3$ is added to convert the insoluble potassium bitartrate shown in the equation into soluble $KNaC_4H_4O_6$, and to combine with the free antimonic and hydriodic acids also produced.

VIII. STANDARD SOLUTION OF SODIUM THIOSULPHATE ("HYPO").

Strength: $\frac{N}{10}$ = 24·764 (24·8) *Gm.* $Na_2S_2O_3 . 5H_2O$ *per* 1000 *Cc.*

(*A*) Preparation and Check.

Dissolve 30 Gm. of crystallized sodium thiosulphate (hyposulphite) in sufficient water to make 1100 Cc. at 15° C. Put 10 Cc. of this "crude hypo" into a flask, add a little starch mucilage, and titrate with decinormal iodine until a faint permanent blue is obtained. Note the number of Cc. of iodine used, and make every 10 Cc. of the "crude hypo" up to this bulk with distilled water. Suppose, for example, 10 Cc. of "crude hypo" took 10·8 Cc. $\frac{N}{10}$ iodine, and we had 1080 Cc. of the crude solution left, then—

$$\frac{1080 \times 10·8}{10} = 1166·4 \text{ Cc. of correct } \frac{N}{10} \text{ "hypo."}$$

50 Cc. of the finished solution must be again titrated, and must take 50 Cc. of $\frac{N}{10}$ iodine. It must be kept in dark amber colored bottles and carefully protected from dust. Each Cc. will contain ·024764 (·0248) real $Na_2S_2O_3 . 5H_2O$.

Decinormal "hypo" deteriorates rapidly, even under the most favorable circumstances, and must therefore be checked against $\frac{N}{10}$ iodine each day it is used, and any deficiency found allowed for in the calculations. Thus, suppose we checked our "hypo" as above explained, and found that 20 Cc. of it only took 19 Cc. of iodine, and then we used the same "hypo" in an analysis which absorbed 40 Cc., we would correct thus:—

$$\frac{19 \times 40}{20} = 38 \text{ Cc. real } \frac{N}{10} \text{ "hypo" actually absorbed;}$$

and then 38 × Cc. equivalent of substance analyzed gives the amount thereof present.

Practical analysts, knowing that they must always check in any case, always titrate with the "crude hypo," and do not trouble to make it exactly $\frac{N}{10}$, preferring simply to make a calculated correction on every analysis, as indicated by the check for the day previously done against $\frac{N}{10}$ iodine.

Solution of sodium thiosulphate is used as follows :—

(*B*) Estimation of Free Iodine.

By weighing out ·32 Gm., dissolving in a little water by the aid of 1 Gm. potassium iodide, and then running in "hypo" till the color is reduced to that of a pale sherry; lastly, adding starch mucilage, and going on till the blue produced by the starch is just bleached. Then by the equation,

$$2(Na_2S_2O_3 . 5H_2O) + I_2 = 2NaI + Na_2S_4O_6 + 10H_2O,$$

it is evident that each Cc. $\frac{N}{10}$ "hypo" = ·012653 (·0127) iodine.

(*C*) Estimation of Free Chlorine or Bromine.

For *chlorine water.*

Weigh 17·7 Gm. from a stoppered bottle, pouring it directly into a flask containing 2 Gm. of potassium iodide previously dissolved in 50 Cc. of water, and then titrate with "hypo" as already described under (*B*).

The Cl first liberates an equivalent quantity of iodine from the KI, and the "hypo" then acts upon the I_2 so set free, thus :—

$$Cl_2 + 2KI = 2KCl + I_2.$$
$$2(Na_2S_2O_3 . 5H_2O) + I_2 = 2NaI + Na_2S_4O_6 + 10H_2O.$$

Therefore each Cc. $\frac{N}{10}$ "hypo" = ·003537 (·00355) chlorine.

On the same principle we would titrate *bromine water*, but in that case each Cc. $\frac{N}{10}$ "hypo" would = ·007976 (·008) bromine.

(*D*) Estimation of Available Chlorine.

For *chlorinated lime* and its solution.

Weigh ·354 Gm. of the solid or 5 Gm. of the *liquor*. Triturate the weighed solid with 50 Cc. water, and wash the whole carefully into a flask. Then add ·8 Gm. of KI and 5 Cc. diluted HCl. Lastly, titrate with "hypo," adding starch mucilage towards the end of the titration as already described under (*B*). Then by the equations,

$$(a)\ CaOCl_2 + 2HCl = CaCl_2 + H_2O + Cl_2,$$
$$(b)\ Cl_2 + 2KI = 2KCl + I_2,$$
$$(c)\ 2(Na_2S_2O_3 . 5H_2O) + I_2 = 2NaI + Na_2S_4O_6 + 10H_2O,$$

we come to the result already shown for chlorine water—namely, that

$$2(Na_2S_2O_3 . 5H_2O) = I_2 = Cl_2.$$

Therefore each Cc. $\frac{N}{10}$ "hypo" = ·003537 (·00355) Gm. "*available chlorine*" in all chlorinated compounds.

Liquor sodæ chlorinatæ.

Use 6·7 Gm., and proceed as for chlorinated lime. The action and calculations are the same, only differing in the first equation, which is :—

$$Na_2OCl_2 + 2HCl = 2NaCl + H_2O + Cl_2.$$

(*E*) Estimation of Iron in Ferric Salts.

When excess of potassium iodide is added to a ferric salt in solution in the presence of hydrochloric acid, and the whole is digested at 40° C. in a closely stoppered bottle for half an hour, the iron in the ferric salt is reduced to the ferrous state, and an equivalent quantity of iodine is liberated. Thus, taking ferric chloride, we would have :—

$$Fe_2Cl_6 + 2KI = 2FeCl_2 + 2KCl + I_2.$$

Therefore each atom of iron so reduced liberates 1 atom of iodine, and then the iodine so liberated is titrated with $\frac{N}{10}$ "hypo"; and thus we see—

$$Na_2S_2O_3 . 5H_2O = I_2 = Fe_2.$$

And so each Cc. of $\frac{N}{10}$ "hypo" = ·005588 (·0056) iron in the ferric salt under analysis.

In practise we weigh ·56 Gm. of a solid ferric salt, or 1·12 Gm. of a ferric *liquor*, put it into a stoppered bottle of about 100 Cc. capacity, dissolve in or dilute with 15 Cc. of water, add 2 Cc. of hydrochloric acid and 1 Gm. of potassium iodide, and quickly close the bottle. The whole is then placed in a basin of water heated to 40° C. (104 F.), and maintained at that temperature for half and hour. At the expiration of that time the bottle and contents are cooled to 15° C., and starch mucilage having been added, the contents are titrated in the bottle with $\frac{N}{10}$ "hypo." The number of Cc. of "hypo" used (after correction for check if necessary) are then multiplied by the Cc. equivalent of iron as above given. The point of the process is to get no loss of iodine vapour during the heating, and yet to take care that the bottle does not burst by the expansion of the contained air by the heat. When ·56 Gm. of a ferric salt is taken, each Cc. of $\frac{N}{10}$ "hypo" used = 1 per cent. of iron; but when 1·12 Gm. of a liquor is started with, then each Cc. = ·5 per cent. of iron.

IX. STANDARD SOLUTION OF BROMINE.

Strength: $\frac{N}{10}$ = 7·976 (8·000) *Gm. per* 1000 *Cc.*

(*A*) Preparation and Check.

As it is impossible to keep an actual solution of bromine, we make and keep a mixed one of a bromide and bromate in such proportion that when acidulated with a fixed quantity of acid (5 Cc. HCl) shall give a definite amount of free bromine by the equation—

$$5KBr + KBrO_3 + 6HCl = 6KCl + 3Br_2 + 3H_2O.$$

To do this we follow the procedure of the U.S.P. as follows :—

Dissolve 3 Gm. of sodium bromate and 50 Gm. of sodium bromide (or 3·2 Gm. of potassium bromate and 50 Gm. of potassium bromide) in enough water to make, at or near 15° C., 900 Cc. Of this solution transfer 20 Cc., by means of a pipette, into a bottle having a capacity of about 250 Cc., provided with a glass stopper; add 75 Cc. of water, next 5 Cc. of pure hydrochloric acid, and immediately insert the stopper. Shake the bottle a few times, then remove the stopper just sufficiently to quickly introduce 5 Cc. 20 per cent. solution of potassium iodide, taking care that no bromine vapor escape, and immediately stopper the bottle. Agitate the bottle thoroughly, remove the stopper and rinse it and the neck of the bottle with a little water so that the washings flow into the bottle, and then add from a burette $\frac{N}{10}$ sodium hyposulphite until the iodine tint is exactly discharged, using towards the end a few drops of starch indicator. Note the number of Cc. of the sodium hyposulphite thus consumed, and then dilute the bromine solution so that equal volumes of it and of $\frac{N}{10}$ sodium hyposulphite will exactly correspond to each other under the conditions mentioned above.

EXAMPLE. Assuming that the 20 Cc. of the bromine solution have required 25·2 Cc. of the hyposulphite to completely discharge the iodine tint, the bromine solution must be diluted in the proportion of 20 to 25·2. Thus, if 850 Cc. of it are remaining, they must be diluted with water to measure 1071 Cc.

After the solution is thus diluted, a new trial should be made in the manner above described, in which 25 Cc. of the $\frac{N}{10}$ sodium hyposulphite should exactly discharge the tint of the iodine liberated by the bromine set free from the 25 Cc. of bromine solution.

Keep the solution in dark amber-colored glass-stoppered bottles.

(*B*) Estimation of Carbolic Acid (Phenol).

The bromine solution is added in fixed excess, more than sufficient to convert all the phenol into insoluble **tribromophenol**—$C_6H_2Br_3 . OH$—and the bromine remaining undecomposed is titrated with KI, starch, and $\frac{N}{10}$ "hypo" as above described. The number of Cc. of "hypo" used having been deducted from the Cc. of $\frac{N}{10}$ bromine started with, the difference × ·001563 = real phenol present in the amount of sample weighed out for analysis. The following example is taken from the U.S.P.:—

Valuation of Carbolic Acid. Dissolve 1·563 Gm. of the carbolic acid to be valued in a sufficient quantity of water to make 1000 Cc. Transfer 25 Cc. of this solution (containing 0·039 Gm. of the acid) to a glass-stoppered bottle having a capacity of about 200 Cc., add 30 Cc. of $\frac{N}{10}$ bromine (which is 5 Cc. more than would be required if the carbolic acid in the solution were absolute phenol, the excess being added to promote the formation and separation of tribromophenol), then 5 Cc. of hydrochloric acid, and immediately insert the stopper. Shake the bottle repeatedly in the course of half an hour, then remove the stopper just sufficiently to introduce quickly 5 Cc. of a 20 per cent. aqueous solution of potassium iodide, being careful that no bromine vapor escape, and immediately stopper the bottle. Shake the latter thoroughly, remove the stopper and rinse it and the neck of the bottle with a little water so that the washings may flow into the bottle, and then add from a burette $\frac{N}{10}$ sodium hyposulphite until the iodine tint is exactly discharged, using towards the end a few drops of starch indicator. Note the number of Cc. of $\frac{N}{10}$ sodium hyposulphite consumed. Deduct this from 30 (the number of Cc. of bromine originally added), and multiply the remainder by 4. The product will, approximately, represent the percentage of absolute phenol in the carbolic acid tested. For accurate work the remainder is multiplied by ·001563, and the result calculated to percentage on the ·039 Gm. of acid taken.

X. ANALYSIS BY DIRECT OXIDATION.

(*A*) General Principles.

The two chief direct oxidizers employed in analysis are potassium permanganate and potassium bichromate, both of which part with oxygen in presence of sulphuric acid, but in different proportions. These actions are represented by the following equations:—

With bichromate. $K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + O_3$;

therefore each *molecular weight* of bichromate gives *three atomic weights* of oxygen.

With permanganate. $K_2Mn_2O_8 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + O_5 + 3H_2O$;

therefore each *molecular weight* of permanganate gives *five atomic weights* of oxygen.

We have already seen that the *theoretical* N solution of hydrogen is 1 Gm. per 1000 Cc., or ·001 in each Cc.; and looking to the formula of the simplest compound of H and O, namely water, we notice that 1 atom O combines with 2 atoms H. It therefore follows that 1 Gm. of H would combine with

15·96 (16) ÷ 2 = 7·98 (8) Gm. of O. A *theoretical* N solution of O would thus be 7·98 (8) Gm. per 1000 Cc., and a $\frac{N}{10}$ solution would be ·798 (·8) Gm. O per 1000 Cc., and would contain ·000798 (·0008) oxygen in each Cc. In oxidation analysis, therefore, *a $\frac{N}{10}$ solution of any oxidant is that weight in Gm. per 1000 Cc. which will give off ·798 (·8) Gm. oxygen under the conditions in which it is used.*

Thus taking *bichromate* we have

$$K_2Cr_2O_7 = 293·78 \div 6 = 4·896 \text{ Gm. per 1000 as a } \tfrac{N}{10} \text{ oxidant;}$$

and for *permanganate* we have

$$K_2Mn_2O_8 = 315·34 \div 10 = 3·1534 \text{ Gm. per 1000 as a } \tfrac{N}{10} \text{ oxidant.}$$

Each Cc. of either of these solutions will give ·000798 (·0008) available oxygen, and will therefore produce exactly the same effect in the analysis of anything readily oxidized.

Oxidants are never employed in stronger solution than $\frac{N}{10}$, and frequently for delicate work they are made centinormal ($\frac{N}{100}$).

There are almost unlimited cases in which such solutions may be applied to the various bodies capable of undergoing a definite change by oxidation, but the most common applications are :—

(1) *For the estimation of ferrous salts.* If we look at the simplest equation for the transference of iron from the ferrous to the ferric state, we find

$$2FeO + O = Fe_2O_3.$$

So we observe that 1 atomic weight of O can oxidize 2 atomic weights of Fe, or that

$$\frac{O}{2}\ 7·98\ (8) = Fe\ 55·88\ (56);$$

therefore each Cc. of $\frac{N}{10}$ oxidant = ·005588 (·0056) metallic iron or $\frac{\text{molecular weight}}{10,000}$ of any ferrous salt containing 1 atom of iron in its molecule. Either of the oxidants may be employed for the estimation of ferrous salts.

Take, for example, *crystallized ferrous sulphate.* We have the equations :—

With bichromate.

$$K_2Cr_2O_7 + 6FeSO_4.7H_2O + 7H_2SO_4 = 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 49H_2O.$$

With permanganate.

$$K_2Mn_2O_8 + 10FeSO_4.7H_2O + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 78H_2O.$$

In certain ferrous salts, such as *phosphate* or *arseniate*, the molecules of which contain Fe_3, it is evident that from the equation

$$K_2Cr_2O_7 + 2Fe_3(AsO_4)_2 + 7H_2SO_4 = Fe_2(SO_4)_3 + 2Fe_2(AsO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$$

each Cc. of $\frac{N}{10}$ oxidant would equal $\frac{\text{molecular weight} \times 3}{10,000}$ of such salt.

Such salts are included in the B.P., but not in the U.S.P.

The following table gives the equivalents of 1 Cc. of either oxidant for some of the more important ferrous salts :

Name and formula	Gm to weigh.	Accurate equivalent.	Approximate equivalent.
Iron (in ferrous salts) Fe	-	·005588	·0056
,, (in reduced iron) Fe	·056	·005588	·0056
Ferrous carbonate (in ferr. carb. sacch.) $FeCO_3$	1·16	·011573	·0116
,, sulphate (cryst.) $FeSO_4.7H_2O$	1·39	·027742	·0278
,, ,, anhydrous $FeSO_4$	·76	·015170	·0152
,, ,, (dried U.S.P.) $2FeSO_4 + 3H_2O$	·895	·017864	·0179
,, phosphate B.P. $Fe_3(PO_4)_2.8H_2O$	·836	·010733	·0167
,, arseniate B.P. $Fe_3(AsO_4)_2$	·744	·014807	·0149

(2) *For the estimation of oxalic acid and oxalates.* The following equation

shows that to oxidize oxalic acid or an oxalate requires 1 atomic weight of oxygen for each molecule of oxalate :—

$$H_2C_2O_4 . 2H_2O + O = 2CO_2 + 3H_2O ;$$

therefore each Cc. of a $\frac{N}{10}$ oxidant will equal $\frac{H_2C_2O_4 . 2H_2O}{20,000}$ or ·006285 (·063) equivalent to each Cc. The only oxidant employed in this case is permanganate.

(3) *For the estimation of hydrogen dioxide and peroxides.* By the equations

$$H_2O_2 + O = H_2O + O_2,$$
$$BaO_2 + O = BaO + O_2,$$

it is evident that 1 atomic weight of O acts with 1 molecular weight of the peroxide; therefore 1 Cc. $\frac{N}{10}$ oxidant $= \frac{\text{molecular weight}}{20,000}$, the only oxidant used in this case being permanganate. The following are the equivalents :—

Name and formula.	Accurate equivalent.	Approximate equivalent.
Hydrogen dioxide (in solution) H_2O_2 . . .	·001696 .	. ·0017
Barium dioxide BaO_2	·008441 .	. ·00845

(4) *For the estimation of hypophosphorous acid and hypophosphites.* The equation

$$HPH_2O_2 + O_2 = HPO_3 + H_2O$$

shows that each molecular weight of hypophosphorous acid requires 2 atomic weights of oxygen; therefore each Cc. $\frac{N}{10}$ oxidant $= \frac{\text{molecular weight}}{40,000}$. The only oxidant used in this case is permanganate, and the following table gives the usual information :—

Name and formula.		Gm. to weigh.	Accurate equivalent.	Approximate equivalent.
Hypophosphorous acid	HPH_2O_2 . .	·5 .	. ·001647 .	. ·00165
Sodium hypophosphite	$NaPH_2O_2$.	·1 .	. ·002646 .	. ·00265
Potassium ,,	KPH_2O_2 . .	·1 .	. ·002598 .	. ·0026
Calcium ,,	$Ca(PH_2O_2)_2$.	·1 .	. ·0021209 .	. ·00213
Ferric ,,	$Fe_2(PH_2O_2)_6$.	·1 .	. ·0020877 .	. ·00209

(5) *For equivalent liberation of halogens from haloid salts.* The equation

$$2KI + O + H_2O = 2KHO + I_2$$

shows that each atomic weight of nascent oxygen can liberate 2 atomic weights of a halogen from its salts; therefore each Cc. of $\frac{N}{10}$ oxidant can liberate $\frac{\text{atomic weight}}{10,000}$ of the halogen. Thus each Cc. of $\frac{N}{10}$ permanganate is equivalent to ·003537 (·00355) **Cl**, ·007976 (·008) **Br**, or ·012653 (·0127) **I**.

The liberated halogen is then estimated by means of $\frac{N}{10}$ sodium thiosulphate (" hypo ") as already described.

(*B*) Preparation and Uses of Solution of Potassium Permanganate.

Strength: $\frac{N}{10}$ = 3·1534 (3·15) *Gm.* $K_2Mn_2O_8$ *in* 1000 *Cc.*

(1) Preparation and Check.

(*a*) *Solution for immediate use.* Dissolve 3·5 Gm. $K_2Mn_2O_8$ in 1000 Cc. of recently boiled and cooled distilled water. This is the crude solution, and must now be checked by placing 10 Cc. $\frac{N}{10}$ oxalic acid in a small flask, adding 1 Cc. of pure strong sulphuric acid, and titrating this liquid while hot with the crude solution (over a sheet of white paper) till a faint permanent pink is obtained. Note the number of Cc. of solution used, and dilute the remainder of the crude solution with similarly treated water until 50 Cc. exactly correspond to 50 Cc. $\frac{N}{10}$ oxalic acid.

Thus, if 10 Cc. $\frac{N}{10}$ oxalic took 9·2 Cc. crude permanganate, we would have 920 Cc. up to 1000 Cc., and then we would (after confirmation of 50 Cc against 50 Cc. acid) have true $\frac{N}{10}$ permanganate. This solution cannot be depended on unless just made, and if a solution is to be made and stocked more precautions must be taken. These precautions are so well explained in U.S.P. that the directions therein given cannot be improved, and they are as follows:—

(*b*) *Preparation of $\frac{N}{10}$ permanganate for stock.* Place 3·5 Gm. of pure, crystallized potassium permanganate in a flask, add 1000 Cc. of boiling water, and boil until the crystals are dissolved. Close the flask, and set it aside for two days, so that any suspended matters may deposit. This is the *stronger solution*. Prepare another, *weaker solution*, in the same manner, using 6·6 Gm. of the salt and 2200 Cc. of water, and set this also aside for two days. After the lapse of this time, pour off the clear portion of each solution into separate vessels provided with glass stoppers, and then proceed to test each separately. Introduce into a flask 10 Cc. of $\frac{N}{10}$ oxalic acid, add 1 Cc. of pure, concentrated sulphuric acid, and, before this mixture cools, gradually add from a burette small quantities of the weaker permanganate solution, shaking the flask after each addition and reducing the flow to drops towards the end of the operation. When the last drop of the permanganate solution added is no longer decolorized, but imparts a pinkish tint to the liquid, note the number of Cc. consumed. In the same manner ascertain the titer of the stronger solution, and likewise note down the number of Cc. of the latter consumed. Finally, mix the two solutions in such proportions that 50 Cc. of the mixture will exactly correspond to an equal volume of $\frac{N}{10}$ oxalic acid.

Note.—To obtain the accurate proportions for mixing the two solutions, deduct 10 from the number of Cc. of the weaker solution required to decompose 10 Cc. of $\frac{N}{10}$ oxalic acid. With this difference multiply the number of Cc. of the stronger solution required for the same purpose. The product shows the number of Cc. of the *stronger solution* needed for the mixture. Next deduct the number of Cc. of the stronger solution required to decompose 10 Cc. of $\frac{N}{10}$ oxalic acid from 10, and with the difference multiply the number of Cc. of the weaker solution required for the same purpose. The product shows the number of Cc. of the *weaker solution* needed for the mixture.

Or, designating by S the number of Cc. of the stronger solution, and by W the number of Cc. of the weaker solution required to decompose 10 Cc. of $\frac{N}{10}$ oxalic acid, the following formula will give the proportions in which the solutions must be mixed:—

Stronger solution : Weaker solution :
$(W - 10)\,S \quad + \quad (10 - S)\,W$

EXAMPLE.—Assuming that 9 Cc. of the stronger (S) and 10·5 of the weaker (W) solution had been required, then, substituting these values in the above-given formula, we obtain:

$(10{\cdot}5 - 10)\,9 + (10 - 9)\,10{\cdot}5,$
or 4·5 + or 10·5,

making 15 Cc. of trial solution.

The bulk of the two solutions is now mixed in the same proportion, 450 Cc. of the stronger and 1050 Cc. of the weaker, or 900 Cc. of the stronger and 2100 Cc. of the weaker solution.

After the mixture is thus prepared, a new trial should be made, when 10 Cc. of the solution should exactly decompose 10 Cc. of $\frac{N}{10}$ oxalic acid. If necessary, a new adjustment should be made to render the correspondence perfect.

This solution should be kept in small, dark amber-colored and glass-stoppered bottles (or in bottles provided with tubes, especially designed for the purpose). Thus prepared, this solution will last for months; yet it should be tested occasionally, and, when it is found reduced, the liquid should be brought back to normal strength by the addition of such an amount of the stronger solution as may be determined in the manner above described.

(*c*) *Standardization of crude permanganate solution by a ferrous salt.* Many persons prefer this method to that already given above with oxalic acid. The salt employed in *ferrous ammonium sulphate*, $FeSO_4.(NH_4)_2SO_4.6H_2O$ (= 392), which contains practically $\frac{1}{7}$ of its weight of metallic iron. The process is performed by weighing out 0·7 Gm. of ammonio-ferrous sulphate (= 0·1 Gm. real Fe), dissolving it in 100 Cc. of distilled water, acidulating with 6 Cc. of dilute sulphuric acid (1 to 5), and then titrating with the permanganate until a slight permanent pink is produced, not disappearing on shaking. To see the color, a sheet of white paper should be placed under the flask containing the iron solution, and, at the conclusion of the process, the number of Cc. having been noted, the solution is diluted, on the usual principles, until it takes exactly 17·85 Cc. to oxidize 0·1 Gm. Fe.

(2) Estimation of Ferrous Salts.

Weigh out a proper amount of the ferrous salt, dissolve in 25–50 Cc. water, acidulate with 6 Cc. diluted sulphuric acid (1 to 5), place the flask over a sheet of white paper, and titrate with $\frac{N}{10}$ permanganate till a faint permanent pink is produced. Note the number of Cc. used, and multiply by the Cc. equivalent of the salt under analysis (see table, p. 124).

(3) Estimation of Oxalic Acid and Oxalates.

This is performed as already described under "preparation and check" of permanganate solution (see p. 125). The great point is that the solution to be analyzed should by sufficiently warm to give off visible steam. The equivalent of oxalic acid has been already given (see p. 125).

(4) Estimation of Hydrogen or Barium Dioxides (Peroxides).

The principle of this estimation has been already explained and the equivalents given on p. 125. The following would be an example of the procedure, as illustrated by the U.S.P. directions for the estimation of barium dioxide, and solution of hydrogen and dioxide respectively:—

(*a*) *Barium dioxide.* If 2·11 Gm. of barium dioxide be dissolved, as completely as possible, in ice-cold water to the volume of 25 Cc., with the aid of 7·5 Cc. of phosphoric acid, and 5 Cc. of this solution (corresponding to 0·422 Gm. of the dioxide) be measured off for assay, it should require not less than 40 Cc. of $\frac{N}{10}$ potassium permanganate to impart to the liquid a permanent pink tint, corresponding to not less than 80 per cent. of pure barium dioxide (each Cc. of the volumetric solution indicating 2 per cent. of the latter).

(*b*) *Valuation of solution of hydrogen dioxide.* Dilute 10 Cc. of the solution with water to make 100 Cc. Transfer 17 Cc. of this liquid (containing 1·7 Cc. of the solution) to a beaker, add 5 Cc. of diluted sulphuric acid, and then from a burette $\frac{N}{10}$ potassium permanganate, until the liquid just retains a faint pink tint after being stirred. Each Cc. of the $\frac{N}{10}$ potassium permanganate corresponds to 0·0017 Gm. of absolute hydrogen dioxide.

To express the strength of any solution of hydrogen dioxide approximately in *volumes of available oxygen* (that is, in volumes of oxygen, given off by one volume of the solution upon decomposition), multiply the number of Cc. of $\frac{N}{10}$ permanganate decolorized by 1 Cc. of the solution by 0·56 (0·5594), or those decolorized by 1·7 Cc. of the solution by 0·33. [It is assumed that 1000 Cc. of oxygen, at 0° C. (32° F.) and 760 Mm. pressure, weigh 1·43 Gm.]

To express the strength in *percentage (by weight) of absolute hydrogen dioxide*, multiply the number of Cc. of $\frac{N}{10}$ permanganate decolorized by 1 Cc. of it by 0·17, or divide the number of Cc. of permanganate decolorized by 1·7 Cc. of it by 10.

(5) Estimation of Hypophosphorous Acid and Hypophosphites.

This is done by *residual titration*. Excess of $\frac{N}{10}$ permanganate is added, and the number of Cc. remaining unreduced is found by means of oxalic acid. In practise ·5 Gm. of the free acid is mixed with 7 Cc. H_2SO_4 and 35 Cc. $\frac{N}{10}$ permanganate, and the whole having been boiled for 15 minutes, the excess of permanganate is titrated with $\frac{N}{10}$ oxalic acid till just colorless. If, now, 4·7 Cc. of oxalic acid be used, we have :—

35 − 4·7 = 30·3 Cc. $\frac{N}{10}$ permanganate actually reduced by the hypophosphorous acid, and 30·3 × ·00165 = ·049995, or practically ·05 = 10 per cent. real acid.

For hypophosphites we use the following quantities dissolved in 10 Cc. water :—

	Taken.	H_2SO_4 added.	$\frac{N}{10}$ permanganate added.
Calcium hypophosphite	·1	10 Cc.	50 Cc.
Potassium ,,	·1	7·5 ,,	40 ,,
Sodium ,,	·1	7·5 ,,	40 ,,
Ferric ,,	·1	10 ,,	50 ,,

The above are the methods of U.S.P., but British analysts prefer to ascertain the residual permanganate by adding excess of KI, and then titrating the iodine liberated by $\frac{N}{10}$ "hypo," when each Cc. of "hypo" used = 1 Cc. of residual permanganate, to be deducted from the volume in Cc. originally added, and the difference and the hypophosphite "Cc. equivalent" = the weight present.

(*C*) Preparation and Uses of Solution of Potassium Bichromate.

Strength : $\frac{N}{10}$ = 4·896 (4·9) *Gm.* $K_2Cr_2O_7$ *in* 1000 *Cc.*

(1) Preparation.

Dissolve 4·896 Gm. *pure* potassium bichromate in enough distilled water to make exactly 1000 Cc. at 15° C. (59° F.).

Note.—Pure $K_2Cr_2O_7$, in addition to ordinary tests, should (according to the U.S.P.) conform to the following tests :—In a solution of 0·5 Gm. of the salt in 10 Cc. of water rendered acid by 0·5 Cc. of nitric acid, no visible change should be produced either by barium chloride (absence of *sulphate*) or by silver nitrate (absence of *chloride*). In a mixture of 10 Cc. of the aqueous solution (1 in 20) with 1 Cc. of ammonia water, no precipitate should be produced by ammonium oxalate (absence of *calcium*).

(2) Uses.

(*a*) *For the estimation of ferrous salts.* An appropriate quantity of the ferrous salt is weighed and dissolved in a flask in 50 Cc. of warm distilled water if soluble, or, if insoluble, dilute H_2SO_4 is added till the salt dissolves. While this is proceeding a white porcelain slab is dotted over with drops (from a glass rod) of potassium ferricyanide indicator (see p. 106); the contents of the flask are then acidified with 10 Cc. of dilute H_2SO_4 (1 to 5), and titrated with the $\frac{N}{10}$ bichromate till a drop taken from the flask on the end of a glass rod and touched on one of the spots of the indicator on the slab just ceases to give any blue, thus showing that all the iron has been oxidised from the *ferrous* to the *ferric* state. The number of Cc. $\frac{N}{10}$ bichromate used × the Cc. equivalent of the salt under analysis (see table, p. 124) gives the weight thereof present in the amount taken for analysis. The process should be conducted rapidly to avoid spontaneous oxidation as far as possible. When applied to metallic iron or *ferrum redactum*, the metal should be dissolved in diluted H_2SO_4 in a flask fitted with a cork, through which passes a narrow tube to admit the outward passage of the hydrogen evolved and to prevent ingress of air. With ferrous phosphate and saccharated ferrous carbonate, it is better to replace sulphuric acid by hydrochloric acid and phosphoric acid respectively.

(*b*) ***For alkalimetry.*** Solution of bichromate is sometimes employed to set the strength of volumetric solutions of alkalies. In this case the strength is not based upon the oxygen evolved with acid, but upon the following equation:—

$$K_2Cr_2O_7 + 2KHO = 2K_2CrO_4 + H_2O.$$

Therefore ½ molecular weight $K_2Cr_2O_7$ = 1 molecular weight of KHO, *i.e.*

$$K_2Cr_2O_7 \,.\, 293{\cdot}78\ (294) \div 2 = 146{\cdot}89\ (147) = 55{\cdot}99\ (56)\ \text{KHO}.$$

For alkalimetry, therefore, a decinormal bichromate solution would be made by dissolving 14·689 $K_2Cr_2O_7$ in water at 15° C. to 1000 Cc., and each Cc. of such solution would neutralize ·0056 KHO or ·004 NaHO. If, therefore, we set 50 Cc. of this alkalimetric $\frac{N}{10}$ bichromate against 50 Cc. of alkali, the latter will be correct $\frac{N}{10}$, and any acid in turn set against that would also be $\frac{N}{10}$. The indicator used is phenol-phthalein, as in ordinary alkalimetry. This is a very useful method of standardizing volumetric alkali when we are not absolutely certain of the purity of our oxalic acid. The alkali, however, cannot be made stronger than $\frac{N}{10}$, because 147 Gm. of $K_2Cr_2O_7$ would not dissolve in 1000 Cc. of water, and therefore it is no use for normal alkalies.

(*c*) *For equivalent liberation of halogens.* The $\frac{N}{10}$ bichromate (as oxidant) can do the same work in this respect as the $\frac{N}{10}$ permanganate, and on the same principles. The process is done in presence of sulphuric acid, and the liberated iodine is titrated with $\frac{N}{10}$ "hypo."

XI. FEHLING'S STANDARD SOLUTION OF COPPER.

(*A*) Manufacture and Check by the Ordinary Method.

This solution is used for the estimation of sugars, and is made in two parts, as follows:—

No. 1.

Take of

Sulphate of copper	346·4 grains or 34·64 Gm.
Distilled water	a sufficiency.

Dissolve the sulphate of copper in a portion of the water, and dilute the solution with more of the water to the volume of 5000 grain-measures, or 500 Cc.

No. 2.

Take of

Caustic soda	1¾ ounce or 76·5 Gm.
Tartarated soda	4 ounces or 175·0 Gm.
Distilled water	a sufficiency.

Dissolve the caustic soda and tartarated soda in a portion of the water, and dilute the solution with more of the water to 5000 grain-measures, or 500 Cc.

When required for use, mix equal volumes of the solutions No. 1 and

No. 2. On heating the liquid in a test-tube to boiling, it should remain perfectly clear. Each 10 Cc. of this liquid will represent—

Glucose	·050 Gm.
Maltose	·0807 „
Lactose	·0678 „
Inverted cane sugar	·0475 „
Inverted starch	·045 „

To check Fehling's solution, weigh out ·475 Gm. of pure sugar-candy and dissolve it in 100 Cc. of water in a small flask; add 3 drops of strong HCl, and boil briskly for ten minutes to invert the cane sugar into glucose. Let it cool, neutralize with KHO, and then make up exactly to 100 Cc. with distilled water. Place this liquid in a burette arranged over a basin placed over the gas, and containing 10 Cc. of Fehling's solution and 50 Cc. of water. When the contents of the basin are boiling, run in the sugar solution until all blue color is destroyed. Then note the number of Cc. of sugar solution used, and whatever that number may be, it will contain the equivalent in sugar of 10 Cc. of "Fehling." If the "Fehling" be correct, 10 Cc. of the standard sugar will be used to entirely precipitate it.

It is usually necessary to do the estimation twice, first roughly and then accurately, using the second time drops of $K_4FeC_6N_6$ acidulated with acetic acid on a slab, as an indicator for the disappearance of the last trace of Cu from solution.

Another way of inverting a solution of cane sugar into glucose is to add one-tenth of its bulk of fuming HCl, heat gradually up to 68° C., and then cool. This is the better method when the solution is to be used for the polariscopic estimation of sugar (*see* Chapter XII.).

(*B*) Manufacture and Check by Pavy's Method.

Cuprous oxide dissolves in ammonia, forming a colorless liquid. Taking advantage of this point, Pavy treats an ammoniacal cupric solution at a boiling temperature with sufficient saccharine solution to exactly discharge the blue color. The advantage of this method over that above described lies simply in the fact that there is no bulky red precipitate to interfere with the ready observation of the end reaction. To prepare the test solution, dissolve 20·4 Gm. of Rochelle salt and the same weight of caustic potash in distilled water; dissolve separately 4·158 Gm. of pure cupric sulphate in more water with heat; add the copper solution to that first prepared, and when cold add 300 Cc. of strong ammonia, and distilled water to 1 liter. The process is conducted as follows: 10 Cc. of the ammoniated cupric solution (= 0·005 Gm. of glucose) are diluted with 20 Cc. of distilled water, and placed in a small flask. This is attached by means of a cork to the nozzle of a burette, fitted with a glass stopcock, and previously filled with the saccharine solution previously diluted to a fixed bulk. The cork of the flask should be traversed by a small bent tube, to permit steam to escape. Now heat the flask until the blue liquid boils. Turn the stopcock in order to allow the saccharine solution to flow into the hot solution (which should be kept at the boiling-point) at the rate of about 100 drops per minute (not more nor much less), until the azure tint is exactly discharged. Then stop the flow, and note the number of Cc. used. That amount of saccharine solution will contain 5 milligrams of glucose. To render the determination as accurate as possible, the solution for analysis should be diluted to such an extent that not less than 4 nor more than 7 Cc. are required to decolorize the solution.

To find the total amount of sugar, multiply 0·005 by the original total bulk (in Cc.) of the sugar solution started with, and divide the product by the number of Cc. of solution used from the burette. To observe easily the exact end reaction, a piece of paper or other white body should be placed behind the flask. Mr. Stokes uses the half of an ordinary opal gas globe fixed in the proper position. If the operator objects to the escape of the waste ammoniacal fumes, they may be conducted by a suitable arrangement into water or dilute acid. For a special apparatus for this purpose see the *Analyst*, vol. xii.

(*C*) **Estimation of Sugar.**

The sugar weighed must not exceed ·5 Gm., and must be dissolved in 100 Cc. of water. If the sugar be either glucose or maltose or lactose, it is titrated directly; but if cane sugar, it is first inverted as above described. By always placing 10 Cc. of "Fehling" in the basin, then whatever number of Cc. of sugar solution we use, that number will contain the equivalent of 10 Cc., and we have only to calculate :—

As No. of Cc. used : Total volume of sugar solution : Equivalent of 10 Cc. "Fehling" of the sugar in question : Real sugar present in the quantity weighed out for analysis.

(*D*) **Estimation of Starch.**

Starch is weighed and boiled in a flask with water containing dilute hydrochloric acid, under an upright condenser, for some hours. It is then cooled, neutralized with potassium hydrate, diluted to a fixed volume (not stronger than 1 in 200), and then the solution so made is titrated into 10 Cc. of "Fehling." A much improved process will be found in Chapter X.

XII. ESTIMATION OF PHOSPHORIC ACID

is performed by means of a standard solution of uranic nitrate in the presence of sodium acetate. The necessary solutions are :—

1. **Standard solution of uranic nitrate,** made by dissolving 70 Gm. in 900 Cc. of water, and then, after ascertaining its strength by performing an analysis of 50 Cc. of the standard phosphate solution, diluting with water so that 50 Cc. will correspond exactly to 50 Cc. of that solution. If absolutely pure uranic nitrate were obtainable, theory requires the solution of 71 Gm. in 1 liter of water to yield a solution which will balance the standard phosphate (each 1 Cc. = ·01 Gm. of P_2O_5).
2. **Standard phosphate solution,** made by dissolving 50·42 Gm. of perfectly pure disodium hydrogen phosphate in 1 liter of water, when each 1 Cc. will equal ·01 Gm. of P_2O_5.
3. A solution of 100 Gm. of sodium acetate and 100 Gm. of acetic acid in water, and the whole diluted to 1 liter.
4. Finely powdered potassium ferrocyanide.

To perform the process, the solution of the phosphate in about 50 Cc. of water is placed in a basin on the water bath, mixed with 5 Cc. of solution No. 3 (sodic acetate), and No. 1 (uranic nitrate) is run in from a burette, until a drop taken from the basin on to a white plate just gives a brown color, when a little powdered ferrocyanide is cautiously dropped into its center. The number of Cc. of uranic solution used having been noted, the usual calculations are to be applied.

After repeated trials upon 50 Cc. of the standard phosphate solution, so as to thoroughly adjust the strength of the uranic solution, and at the same time accustom the eye to observe the exact moment of the appearance of the brown coloration, the process may be practically applied to **Manures**.

The best method of preparing the solution of the manure is to heat 10 Gm. to dull redness for 15 minutes, and when cold to reduce it to a fine powder in a mortar, and add gradually 10 Gm. of sulphuric acid diluted to 200 Cc. with water. Rinse the whole into a stoppered bottle, and make up with water to 1 liter. Shake up occasionally for an hour, and having then let all settle for three hours, draw off 100 Cc. (= 1 Gm. manure) for analysis. To this add a little citric acid (10 drops of a cold saturated solution), followed by a slight excess of ammonium hydrate. Again acidify with acetic acid, add 10 Cc. sodium acetate solution, and then use the uranic solution as usual. If all these quantities be rigorously adhered to, each Cc. of uranic solution used can without further calculation be taken as indicating 1 per cent. of tricalcium phosphate in the manure.

This process is highly recommended by Mr. Sutton, of Norwich, and elaborate details will be found in his work on Volumetric Analysis.

XIII. STANDARD SOLUTION OF BARIUM CHLORIDE.

Normal = 103·82 *Gm. per* 1000 *Cc. of* $BaCl_2$.

This is used for taking the amount of a soluble sulphate, by adding it to a known weight of the sulphate dissolved in water acidulated with hydrochloric acid, until precipitation ceases. The process, however, is tedious, and the end of the reaction is not sharp, and it is therefore rarely employed. The following is a specimen of the reaction, using magnesium sulphate:—

$$MgSO_4 \,.\, 7H_2O + BaCl_2 = BaSO_4 + MgCl_2 + 7H_2O.$$

Each Cc. of the standard solution equals ·03093 SO_3 or ·04791 SO_4.

The solution is made by dissolving 103·82 Gm. of pure barium chloride dried at 104° C. in 1 liter of water.

XIV. STANDARD MAYER'S SOLUTION.

Made by dissolving 13·546 Gm. of pure mercuric chloride and 49·8 Gm. of potassium iodide in water, and then making up to 1000 Cc.

This solution is used for the estimation of alkaloids, which should be free from any mucilaginous matter and preferably dissolved in a little dilute sulphuric acid. The reagent is added till precipitation ceases, and the exact equivalent for each alkaloid should be practically checked by operating on a known weight of the pure alkaloid, and then *always using the solution under exactly the same conditions in future analysis.* In the author's hands the process has not worked very well, except for the amount of emetine in *ipecacuanha*, which may be rapidly ascertained as follows:—

15 Gm. of ipecacuanha are treated with 1·5 Cc. of dilute sulphuric acid, and sufficient alcohol of 80 per cent. added to make the whole bulk up to 150 Cc. The whole is allowed to stand for 24 hours, and 100 Cc. are decanted off for analysis. The liquid is evaporated until all the alcohol is driven off, and then brought under the burette containing the test solution, which is run in until it ceases to give a precipitate. The final point of the reaction is ascertained by filtering off a drop or two in a watch-glass placed on black paper, and adding a drop of the reagent, when, if no cloudiness appears, the precipitation of the alkaloid is complete. The number of Cc of the test used multiplied by ·0189 gives the amount of alkaloid in 10 Gm. of the sample, which again multiplied by 10 gives percentage.

XV. ANALYSIS BY THE NITROMETER.

(*A*) General Remarks.

This useful instrument is illustrated in fig. 29. It consists of a measuring tube (A) graduated in Cc., having a funnel-shaped cup (C) connected to it by means of the stopcock (D). This cock is a "three-way" one, and according to the direction in which it is turned, it can make connection and discharge the contents of the cup either into the tube A or out in the waste opening at E; or it can make, or quite shut off, all connection between A and the outer air through E. Connected to A by a piece of flexible indiarubber tube is the ungraduated control tube B. The object of the apparatus is the rapid and accurate measurement, at definite temperature and pressure, of gases evolved during any reaction; and it takes its name from the fact that it was first used to measure the nitric oxide given off by the decomposition of nitric acid. If we fill the instrument with a fluid (say mercury) right up to the tap, and having closed the tap D, we lower the tube B and admit a little air through E (by opening and again closing the tap), we will have a volume of gas in the measuring tube which we desire to measure under definite conditions. Then (1) by allowing the instrument to stand until its contents must have assumed the temperature of the room, a thermometer suspended to the stand will give the temperature of the gas. (2) By then raising or lowering the control tube (B), so that the level of the liquid both in it and in the measuring tube is the same, it is evident that the pressure inside A is the same as in the room, and reference to a barometer standing near will give that pressure. It now only remains to read off the volume of the gas in the measuring tube, and having corrected it to N.T.P. (see page 101), to calculate its weight in Gm. from its volume in Cc., by multiplying the number of Cc. of volume at N.T.P. by the weight of 1 Cc. of the gas in Gm. This latter is obtained by multiplying ·0896 Gm. by *half* the *molecular* weight of the gas, and then dividing by 1000. Suppose, for example, that we have obtained 20 Cc. of nitric oxide at 15° C. and 750 Mm. barometer, and we require to know the weight of NO so got, we should say:—

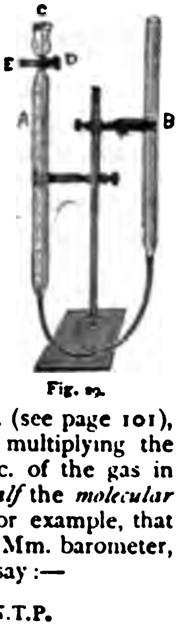

Fig. 29.

(*a*) $\frac{(273 + 0) \times 750 \times 20}{(273 + 15) \times 760} = 18·788$ Cc., corrected volume at N.T.P.

(*b*) $\frac{·0896 \times 15}{1000} = ·001344$ Gm., weight of 1 Cc. NO.

(*c*) $18·788 \times ·001344 = ·0253$ Gm., weight of NO found.

The various possible applications of this instrument are so numerous that exhaustive details would be impossible in the present work; but the following should be practised as typical instances of its use:—

(*B*) Estimation of the Strength of Spirit of Nitrous Ether.

The active principle of this drug is ethyl nitrite. Nitrites when mixed with excess of potassium iodide and acidulated with sulphuric acid cause a liberation of iodine, and evolve all their nitrogen in the form of nitric oxide, thus:—

$$C_2H_5.NO_2 + KI + H_2SO_4 = C_2H_5.HO + KHSO_4 + I + NO.$$

The process is thus conducted. The nitrometer is filled with saturated solution of sodium chloride, with which, owing to its density, a strong spirit will not readily mix; 5 Cc. of the sample to be tested is placed in the cup of the nitrometer, and the control tube having been lowered, the spirit is allowed to enter through the tap, taking care that no air gets in at the same time. 5 Cc. of a strong solution of potassium iodide is next allowed to enter, and this is in turn followed by 5 Cc. of dilute sulphuric acid. Effervescence immediately occurs, and if the tube be vigorously agitated at intervals, the reaction completes itself in 10 minutes. The level of the liquid in the control tube of the instrument is adjusted to equal that in the measuring tube, and the volume of nitric oxide is read off and corrected to 15° C. For B.P. purposes it is, however, sufficient to see that the resulting gas at 15·5° C. and 760 Mm. has seven times (or at all events not less than five times) the volume of the spirit started with, but the U.S.P. requires 55 Cc. of gas from 5 Cc. spirit at 15° C. The *least trace* of air allowed to enter with the liquids vitiates the results of the process, because the nitric oxide would be thereby converted into higher oxides of nitrogen. The gas produced should be tested for purity by seeing that it is entirely absorbed by ferrous sulphate solution.

(*C*) Estimation of the Strength of Sodium Nitrite.

Weigh out ·1 Gm. of the salt, and dissolve it in the smallest possible quantity of water. Rinse this into the nitrometer cup, and proceed as in (*B*). A proper sample should yield 32·5 Cc. of gas, which should be entirely absorbed when a strong solution of ferrous sulphate is introduced. The U.S.P. takes ·15 Gm., and requires 50 Cc. gas at 15° C.

(*D*) Estimation of Nitric Acid in Nitrates.

This depends on the fact that when a nitrate is shaken up with excess of sulphuric acid and mercury the following reaction takes place:—

$$2KNO_3 + 4H_2SO_4 + 3Hg = 3HgSO_4 + K_2SO_4 + 2NO + 4H_2O—$$

thus showing that each molecule of the nitrate radical gives off a molecule of NO. If any chlorides or other haloid salts be present, they are first removed by adding a slight excess of argentic sulphate to the solution and filtering. No quantity of a nitrate exceeding 2 Decigm. should be used, otherwise more gas may be evolved than the instrument will conveniently hold. The nitrometer is charged with mercury, and the nitrate solution, which should not exceed 5 Cc., is put into the cup and passed therefrom into the measuring tube, followed by excess of strong sulphuric acid. The instrument is well agitated for some time, and when action has ceased and the contents have cooled down to the temperature of the room, the level is adjusted and the volume of NO read off and calculated. All the precautions already mentioned must be observed. If any nitrites be present, they affect the accuracy of the estimation, being also decomposed to nitric oxide.

(*E*) Estimation of Soluble Carbonate.

It has been proposed to use the nitrometer for taking the strength of the medicinal solution of ammonium carbonate in the spirit known as *spiritus ammoniae aromaticus*. A given volume of the spirit is placed in the cup and introduced into the nitrometer charged with mercury. This is followed by an excess of dilute hydrochloric acid, and the carbon dioxide evolved by the action of the acid upon the carbonate is measured. The percentage of ammonium carbonate may then be calculated, or an empirical comparison of volume on the principle of that already described for spirit of nitrous ether may be applied. According to Mr. Gravill, the originator of the test, good aromatic spirit of ammonia should give off seven times its volume of carbon dioxide after allowing a correction for the slight solubility of the gas in the liquid with which it is inclosed.

(*F*) Estimation of the Strength of Solutions of Hydrogen Peroxide.

This depends upon the fact that, when hydrogen peroxide acts upon potassium permanganate, acidulated with sulphuric acid, oxygen is evolved. One half of this oxygen is due to the peroxide and the other to the permanganate. The nitrometer should be charged with concentrated solution of sodium sulphate (the B.P. uses brine), and 1 Cc. of the solution introduced from the cup, followed by 12 Cc. of a mixture of 1 Cc. H_2SO_4, 2 Cc. of 5 per cent. solution of $K_2Mn_2O_8$ and 7 Cc. H_2O. The contents of the measuring tube, after the reaction is complete, must remain colored violet, thus showing that sufficient permanganate has been employed. B.P. solution of hydrogen peroxide should, when thus treated, give not less than 18 and not more than 22 times its volume of oxygen.

(*G*) Estimation of Urea in Urine.

This process depends on the fact that when urea is decomposed by an alkaline hypobromite or hypochlorite, it gives off its nitrogen in the free state, the following reaction taking place :—

$$N_2H_4CO + 3NaBrO = 3NaBr + N_2 + CO_2 + 2H_2O.$$

A small flask is fitted with a tight cork, through which passes a funnel tube closed by a clamp and reaching to the bottom of the flask, and also a bent delivery tube just passing through the cork. 5 Cc. of the urine is placed in this flask, and the nitrometer having been filled with water the flask is attached to the tap of the nitrometer at the end E (*see* fig. 29, page 133). 20 Cc. of a solution of bromine in sodium hydrate solution is then placed in the funnel and allowed to run into the urine, and the clamp immediately closed. At the same moment the tap of the nitrometer is so placed as to establish connection between E and the measuring tube. A little warm water in a basin is applied to the flask to hasten the reaction, and when no more gas is evolved, the tap is closed, the temperature and pressure adjusted, and the volume read off as usual. Each Cc. of gas at N.T.P. represents ·0029 Gm. of urea present in the 5 Cc. of urine acted upon.

Fig. 29*a* represents a very simple apparatus that can be improvised in a shop or dispensary. 5 Cc. of urine are placed in the test tube (A), and 20 Cc. of hypobromite solution (or strong *liquor sodæ chlorinatæ* will do as well) into the bottle B. The bottle C is filled with water, and its delivery tube is suspended in a graduated Cc. measure. When all is tight the urine is caused to mix with the reagent by tipping up B, and the gas produced passing into C displaces water, which latter runs into the measure. The number of Cc. of water thus collected in the measure multiplied by ·058 gives the percentage of urea in the urine. It is manifest that 1 fluid dram may be taken, and the measure used may be an ordinary 2 oz. dispensing one (where only English weights and measures are handy), when each fluid dram of water in the measure at the finish will equal 29 per cent. of urea.

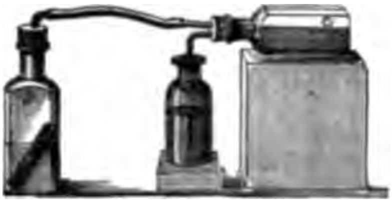
Fig. 29a.

XVI. COLORIMETRIC ANALYSIS.

General Remarks.

This is a variety of volumetric analysis in which the amount of a substance present in solution is found by adding, to a given volume, a fixed quantity of a reagent and observing the color produced. This color is then matched by adding, to an equal volume of distilled water, the same mixed quantity of reagent, and running in a volumetric solution of the pure substance until the same tint is produced. Evidently when this point is reached the amount of substance present in the solution under analysis equals that in the volumetric solution used for the comparative experiment. The applications commonly occurring of this method are:—

(*A*) Estimation of Ammonia by "Nesslerizing."

For this process the following solutions and apparatus are required:—

(*a*) *Nessler's solution.* Dissolve 35 parts of potassium iodide in 100 parts of water. Dissolve 17 parts of mercuric chloride in 300 parts of water. The liquids may be heated to aid solution, but if so must be cooled. Add the latter solution to the former until a permanent precipitate is produced. Then dilute with a 20 per cent. solution of sodium hydrate to 1000 parts; add mercuric chloride solution until a permanent precipitate again forms: allow to stand till settled, and decant off the clear solution. The bulk should be kept in an accurately stoppered bottle, and a quantity transferred from time to time to a small bottle for use. The solution improves by keeping.

(*b*) *Standard ammonia solution.* Dissolve 3·15 Gm. pure ammonium chloride in 1000 Cc. of distilled water free from ammonia. For use, dilute 10 Cc. of this solution to 1000 Cc. with ammonia free distilled water. Each Cc. of the diluted solution will then contain ·01 Milligm. of NH_3 (*i.e.* ·00001 Gm.).

(*c*) *Two narrow cylinders of colorless glass,* of perfectly equal height and diameter, holding about 70 Cc., and graduated at 50 Cc. These should either have a milk glass foot or should stand upon a perfectly white paper.

(*d*) *A pipette* to deliver 2 Cc.

(*e*) *A quantity of ammonia-free distilled water.* This is obtained by placing a liter of ordinary distilled water in a retort, attaching a condenser and distilling until what passes over ceases to give any color with "Nessler's solution." The remaining water in the retort is then cooled and bottled for use.

The liquid in which ammonia is to be estimated (usually a distillate obtained in water analysis) is first made up to a fixed bulk with ammonia-free distilled water, and the bulk noted. It must be so diluted that it only gives a *color* and not a *precipitate* with "Nessler." 50 Cc. of this solution are placed in a cylinder, and 2 Cc. of "Nessler" having been added by the pipette, and the whole stirred with a *perfectly clean rod*, the color produced is observed. A little experience soon teaches the operator to judge the probable amount of ammonia solution required to produce a similar tint. Let us suppose, for example, that the color is judged to be equal to 2 Cc. of ammonia, then we proceed to confirm our idea: 2 Cc. of the standard ammonia solution are run from a burette into the other cylinder, ammonia-free water is added to 50 Cc., then the 2 Cc. of "Nessler," and the whole stirred with the clean rod. If now, after a few minutes, the colors match, we are correct; but if not, then we must try again and again with more or less standard ammonia until we get an exact match between the colors in the two cylinders. This having been attained, the calculation is very simple, and will be best explained by an example. Suppose that we start with a distillate containing ammonia and made up to 200 Cc., and that we employ 5 Cc. of standard ammonia solution in the comparison experiment, to match the color produced by "Nessler" in 50 Cc. of such distillate. Then ·5 Cc. × ·01 = ·05, and ·05 × 4 = ·2: therefore the whole 200 Cc. of distillate contained ·2 Milligm. of NH_3. Beginners should train their eyes by observing the colors produced by adding various quantities of standard ammonia to 50 Cc. of ammonia-free water, and then introducing the "Nessler." $\frac{1}{10}$ of a Cc. of standard ammonia will produce a very faint yellow, while larger amounts will increase the color to orange, and finally to deep orange-red. We should always wait 3 minutes before observing, as the full color does not appear under that time, and the temperature of the room should not be below 12° C.

(*B*) Estimation of Nitrites in Water.

See Water Analysis, Chapter X.

(*C*) Estimation of Minute Quantities of Copper or Iron.

This has often to be done in articles of food, such as preserved vegetables. After having been burned, and the ash dissolved in an appropriate acid, a solution is obtained, which is made up to a definite volume. 50 Cc. is treated with a fixed excess of ammonium hydrate in a "Nessler" glass. The same amount of ammonia is added to 50 Cc. of water in another glass, and a very weak standard solution of cupric sulphate is dropped in from a burette until the colors match, and the amount of copper solution used is noted and calculated. Small quantities of ferric iron may also be estimated in the same way by the use of potassium ferrocyanide in the presence of a fixed amount of acidulation with hydrochloric acid, and matching the color by a weak standard solution of ferric chloride. This is often useful in analyzing bread for the presence of alum, when we first weigh the precipitate of aluminium phosphate containing some ferric phosphate, then dissolve it in HCl, find the amount of iron present in this manner, and deduct it, so saving a long separation.

CHAPTER VIII.

GRAVIMETRIC QUANTITATIVE ANALYSIS OF METALS AND ACIDS.

DIVISION I. PRELIMINARY REMARKS.

GRAVIMETRIC quantitative analysis is that method by which the substance to be estimated is converted into some chemically definite compound, weighed as such, and the amount of the original substance obtained from this weight by calculation. The same definite compound will answer both for the estimation of its metal and of its acid. For example, if we precipitate a known weight of argentic nitrate with hydrochloric acid we obtain insoluble argentic chloride, which may be filtered out and weighed, and the amount (x) of Ag in the quantity started with calculated therefrom, because—

$AgCl$: Ag :: weight of $AgCl$ found : x.
142·3 : 107·11 :: „ „ „ : x.

If, on the other hand, we start with a known weight of hydrochloric acid, precipitate it with argentic nitrate, and collect and weigh the argentic chloride formed, we can find the amount (x) of real HCl actually present in quantity started with, because—

$AgCl$: HCl :: weight of $AgCl$ found : x.
142·3 : 36·19 :: „ „ „ : x.

Before giving individual processes for quantitative analysis, we must first say something about the usual manipulation involved, which will serve as general directions, so saving continual repetition of details.

(*A*) The Preparation of Filters.

Ready-cut filters may be procured from the dealers in chemical apparatus. The kind known as Swedish is the best for all cases where the precipitate is finely divided or pulverulent. For gelatinous precipitates, such as ferric hydrate and calcium phosphate, the white English or German filters work more rapidly; but they should never be used, say, for barium sulphate, or calcium oxalate, as those bodies would very likely pass through the pores of the filter, and so cause a loss in the analysis. Whatever paper be employed, the size for quantitative operations is, for the larger sort six inches in diameter, for the smaller, about two inches. The latter size is used where we have to deal with traces of precipitate only, or when a small quantity of fluid has to be filtered. The paper should yield nothing to dilute acids, and if the ash exceed one milligramme per large filter it should be reduced by placing, say, 100 cut filters for some hours in a basin filled with a mixture of one volume of HCl and eight volumes of water. They must be then *repeatedly* washed with distilled water till *quite* free from acidity, otherwise they would crumble to pieces when being folded. The washing is a very tedious operation indeed, and having been completed, the basin is put on to a water bath till the filters are perfectly dry.

(*B*) Estimation of the Ash of Filters.

This is most conveniently done by folding ten filters in a small compass, twisting a long platinum wire round the packet so as to form a cage, holding the free end in the hand and the paper over a previously weighed platinum crucible, while touching it with the flame of a Bunsen burner. The paper burns and the ash drops into the crucible, while any particles of carbon which have escaped combustion are quite consumed by exposing the crucible for some time to a red heat till the ash gets perfectly white. The crucible after cooling is reweighed, and its increase is the ash of ten filters. Divided by 10, we get the ash of one filter; and in every case where both filter and precipitate are burned, the ash of the filter thus found must always be deducted from their total weight, and the difference is then the actual weight of the precipitate. Filter papers ready cut and freed, as far as possible, from mineral matter by the action of hydrochloric and hydrofluoric acids can now be purchased. By the use of such papers the filter ash is so reduced that it need not be considered, except in the most delicate investigations.

(*C*) The Collection and Washing of Precipitates.

When the precipitate has been fully formed and the supernatant fluid has become quite clear, the latter is poured on the filter (which is either previously tared or not, according to circumstances), care being taken not to disturb the precipitate. This is done by holding a glass rod in a perpendicular position over the filter, placing the lip of the beaker against it, and causing the liquid to flow steadily down the rod into the filter. When the latter is three-fourths full, the beaker is turned into an erect position and the rod drained against the inside of the lip, and then laid across the top of the beaker until it is time to refill the filter. After thus pouring off as much as practicable, the precipitate remaining in the beaker is treated with water and well stirred. When the whole has once more settled, the clear fluid is again passed through the filter. This operation having been repeated three or four times, the precipitate is allowed to pass on to the filter, any particles which stick to the sides of the beaker being removed with a feather or a rod tipped with a small piece of black india-rubber tubing; and the whole having been thus collected, the washing is continued by means of a washing-bottle (fig. 30), till the precipitate is quite freed from its soluble impurities. For instance, in estimating sulphuric acid, the barium sulphate is washed till the filtrate no longer gives a turbidity with argentic nitrate.

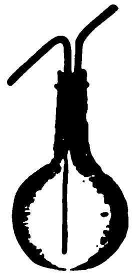
Fig. 30.

Many bodies, as ferric and aluminic hydrate, most phosphates, barium sulphate, and some of the carbonates, are best washed with boiling water. Others, on the contrary, must be washed with cold water, while a few require washing with special mixtures—such as plumbic sulphate, for which we use cold water acidified with some H_2SO_4; magnesium ammonium phosphate, for which cold dilute ammonium hydrate is used, etc.

(*D*) Drying of Precipitates.

After the precipitate has been thoroughly washed and perfectly drained, the funnel containing it is loosely covered over with filter paper and then put into the water oven or air bath till dry. Most precipitates are dried at a temperature of 100° C. (212° F.), but some of them require a heat of 105° C. (220° F.) before becoming constant in weight. Prolonged and repeated drying is only necessary when the precipitate is weighed on the filter, as described below. Fig. 31 shows a water oven for drying at 100° C., while fig. 32 shows an air bath for drying at higher temperatures. This bath is fitted with an apparatus (called a thermostat) for automatically controlling the gas supply, and consequently the temperature.

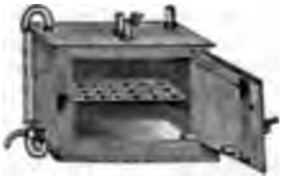

Fig. 31.

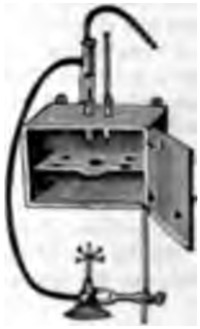

Fig. 32.

(*E*) Igniting and Weighing Precipitates.

Many precipitates must first be ignited before they can be weighed. This is to drive off water, which they may still retain after drying at 100° C., or to reduce them to a more definite condition. For instance, zinc is best weighed as oxide, and therefore the precipitate, consisting of oxycarbonate, is first ignited. Iron is precipitated as hydrate, but the composition of that body not being constant, it is ignited and so made into pure oxide before weighing. As soon, therefore, as the precipitate appears dry, it is carefully detached from the filter and put into a previously ignited and weighed crucible, the filter is burned on the lid (which has been weighed together with the crucible), the ash is thrown into the crucible, and the latter covered with the lid. The crucible is now supported by a pipe-clay triangle, and gently ignited at first, to prevent spurting from the sudden evolution of steam or other gases. The lid is now taken off, and the crucible inclined a little, so as to give a free access of air. The ignition is continued for some minutes, and the crucible, having been again covered with a lid, is allowed to cool in a desiccator and weighed. A desiccator is shown in fig. 33, and will be seen to consist of a glass shade

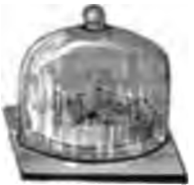

Fig. 33.

Fig. 34.

in which is a vessel containing strong sulphuric acid to keep the air under the glass shade always free from moisture.

The heat of an ordinary Bunsen burner is generally sufficient for all purposes; but the conversion of calcium carbonate into oxide requires the aid of a gas blowpipe; while argentic chloride must only be heated over a rose Bunsen or spirit lamp until it just begins to fuse. The filters are, as already shown, burned separately, to prevent any reduction of the precipitate by the carbon of the filter.

Some precipitates are not ignited, but weighed on a previously tared filter. Before weighing the filter—for which purpose a weighing tube (fig. 34) is used, or the filter is placed between two closely-fitting watch-glasses provided with a clamp to hold them together—it must first be dried for fifteen minutes at 100° C. After drying the precipitate, the filter is again placed in the tube or between the glasses and reweighed: the increase shows, of course, the weight of the substance. It is well to re-place the filter in the bath for, say, half an hour, and to weigh again. Should the weight be considerably less, it must be once more put into the bath and reweighed. Another method of weighing precipitates on a filter is to prepare two filters of equal size, A and B. Cut off the bottom point of B, so that A will go inside it with its point projecting through the opening. Now put B on the weight scale of the balance, and cut off minute slices from the top of A until the two are exactly counterbalanced. Place A inside B, and then, having put both in the funnel, collect the precipitate, wash and dry as usual, and cool under the desiccator. Lastly, detach B, and use it for a tare, putting it into the weight pan, and then the weights required to balance A and its contents will be the weight of the precipitate, because, both filters having been exposed to the same conditions, the tare is accurate.

(*F*) Estimation of Moisture.

A watch-glass is exactly tared on the balance, and then 2 grammes of the substance (in powder, if possible) are carefully weighed upon the glass, and the total weight noted. The glass, with contents, is then placed in the drying oven and heated therein for an hour, at the expiration of which it is removed to the desiccator, and, when cold, is weighed and the weight noted. It is then replaced in the oven for half-an-hour, and the cooling and weighing repeated. If the two weights do not agree within, say, 2 milligrammes, the process is repeated until two concordant weighings are obtained. The weight after drying, deducted from the total weight of glass + substance started with, gives the moisture, which figure multiplied by 50 gives percentage.

(*G*) Estimation of the Ash of Organic Bodies.

This determination is necessary in every analysis of a vegetable or animal substance. A platinum dish is heated to redness, cooled under the desiccator, weighed, and the weight noted. A suitable quantity, say 5 to 10 grammes of the substance, is weighed into the dish, which is then arranged on a triangle support over a Bunsen burner and heated to dull redness. If after fumes cease the substance is seen to have assumed a coke-like form, it is removed from the dish into a small, dry mortar, and having been carefully powdered, the powder is replaced in the dish and maintained at a dull red heat until it has become perfectly white, or at least until all carbon has been burned off. If the burning proves very tedious and the last traces of carbon are very difficult to burn, the addition of a light sprinkling of ammonium nitrate will cause the process to complete itself more rapidly. The dish is now cooled under the desiccator and weighed, and the weight of the empty dish having been deducted, the difference gives the weight of the ash, which is then calculated to percentage. The heat should not be allowed to rise to bright redness, because potassium and sodium chlorides, which are very common constituents of the ash, would be thereby volatilised to some extent and so lost. The estimation of ash soluble in water is frequently of great importance, as showing, when too low, that the article has been tampered with so as to remove its active properties. For example, tea which has been used and redried, or ginger, that has been employed to make ginger essence and then redried and sold would both show great deficiency in this respect. To ascertain the amount of soluble ash, the total ash is extracted with boiling distilled water, filtered, washed, and the filter and contents having been dried, are ignited and weighed; lastly, this weight deducted from that of the total ash, gives the soluble ash.

(*H*) Analytical Factors for Calculating the Results of Analyses.

To save the working out of a rule-of-three sum on the result of each analysis it is customary to employ factors. These are obtained by dividing the weight of the required body by the equivalent weight of the body in the form in which it is precipitated. Thus, supposing we are estimating the amount of argentic nitrate present in a solution containing ·6 gramme of the salt, and have precipitated and weighed the same in the form of argentic chloride, we have :—

$$\frac{\text{Molecular weight of } AgNO_3}{\text{Equivalent weight of } AgCl}\ \frac{168{\cdot}69}{142{\cdot}3} = 1{\cdot}1854, \text{ analytical factor.}$$

It now only remains to multiply this factor by the weight of the precipitat- to obtain the answer. Let us further suppose that the weight of the precipie tate was ·5 gramme, then $1{\cdot}1854 \times {\cdot}5 = {\cdot}59270$ real $AgNO_3$ present in the ·6 gramme taken; then $\frac{{\cdot}59270 \times 100}{{\cdot}6} = 98{\cdot}79$ per cent. real $AgNO_3$ present in the sample.

DIVISION II. GRAVIMETRIC ESTIMATION OF METALS.

I. ESTIMATION OF SILVER.

(*A*) As Argentic Chloride.

(Practise upon ·5 gramme pure $AgNO_3$ dissolved in 100 c.c. H_2O.)

Silver is most conveniently weighed as chloride. The silver solution to be estimated is acidified with nitric acid, and hydrochloric acid is dropped in until no more precipitate forms. It is best to have the solution warm, and to stir till the supernatant liquid has got perfectly clear. The clear fluid is now poured off through a filter, and the chloride is washed by decantation with boiling water (always pouring the washings through the filter) till every trace of acid is removed, and subsequently the whole precipitate is brought upon the filter. The filter and contents are then dried in the water oven, and the chloride transferred into a weighed porcelain crucible, and heated over a low flame till it just commences to fuse. The filter is burned on the crucible lid, and the ash treated with a drop of *aqua regia*, the resulting chloride dried, the lid placed on the crucible, and the whole weighed. The tare of the crucible, lid and filter ash having been deducted, the balance is AgCl, from the quantity weighed out for analysis.

(*B*) As Metal.

(*a*) *In organic salts*, by igniting a weighed quantity of the salt in a tared porcelain crucible, and weighing the ash, which will consist of pure metallic silver.

(*b*) *In alloys*, by *cupellation*, as follows: The weighed alloy is wrapped in lead foil, placed on a little cup or *cupel* made of bone ash, and heated to bright redness in a muffle furnace. The lead oxidises and sinks into the cupel, carrying the impurities with it, and leaving a button of pure silver, which is cooled and weighed.

2. ESTIMATION OF LEAD.

(*A*) As Plumbic Oxide.

(Practise upon ·5 gramme pure plumbic acetate.)

The solution containing the substance to be analysed is precipitated with ammonium carbonate in the presence of a little ammonium hydrate. The precipitated plumbic carbonate is then collected on a small filter, washed, and dried. The dry precipitate is removed as completely as possible from the filter-paper, and introduced into a weighed porcelain crucible. The filter having been burned on the lid, and its ash added to the contents of the crucible, the whole is ignited, cooled, and weighed. By ignition the oxide is formed; and after deducting the weight of the crucible and filter ash, the balance is PbO, from the quantity weighed out for analysis. *Organic salts of lead* require simply to be ignited in a tared porcelain crucible, with free access of air, adding a sprinkling of ammonium nitrate (to prevent reduction to the metallic state), and weighing the resulting PbO.

(*B*) As Plumbic Chromate.

(Practise upon ·5 gramme of plumbic nitrate.)

The solution is mixed with excess of sodium acetate and precipitated with potassium chromate. The precipitate is collected, washed with water acidulated with acetic acid, dried, and ignited in a platinum crucible with the usual precautions. The filter is burned on the lid, treated with a drop or two of nitric acid, dried, and again ignited. The crucible and contents are weighed, and the tare of the crucible having been deducted, the balance is $PbCrO_4$, from the quantity weighed out for analysis.

Lead may also be precipitated as $PbSO_4$, washed with cold and very dilute sulphuric acid, dried, ignited, and weighed as such.

3. ESTIMATION OF MERCURY.

(*A*) As Metal.

(Practise upon 1 gramme of "white precipitate," which should yield 77·5% Hg.)

Take a combustion tube of hard glass, closed at one end, and put in: (1) a little magnesite—$MgCO_3$; (2) the weighed quantity of the mercury salt, mixed with excess of quicklime; (3) a few inches of quicklime; (4) a loose plug of asbestos. Draw out the open end of the tube before the blowpipe and bend it down at a right angle. Give the tube a tap or two on the table to insure a free passage along the upper part for gases, and place it in a combustion furnace, with its open end dipping under the surface of some water in a small flask. Apply heat to the front part of the tube, and go gradually backwards until the whole is heated to redness and the CO_2, given off by the $MgCO_3$, has swept all the mercury vapour out of the tube. The mercury collects as a globule under the water in the basin, and is transferred to a tared watch-glass, perfectly dried by pressure with blotting-paper, and weighed. A similar globule may be obtained by prolonged boiling of the mercury salt with excess of stannous chloride strongly acidulated with HCl, the flask used being connected to an upright condenser to save fumes.

(*B*) As Mercuric Sulphide.

(Practise upon ·5 gramme of mercuric chloride.)

Through the solution of the mercuric salt the current of H_2S is passed till the liquid is saturated. The precipitate is collected on a weighed filter, washed first with water, then with absolute alcohol, and finally, to remove any free sulphur, with a mixture of equal parts of ether and carbon disulphide. After drying at 100° C. and weighing, the balance, after deducting the tare of the filter, is HgS from the quantity weighed out for analysis.

4. ESTIMATION OF CADMIUM.

As Sulphide.

(Practise upon ·5 gramme of $CdCO_3$ dissolved in diluted HCl.)

The solution is precipitated with ammonium hydrate and ammonium sulphide. The cadmium sulphide is collected in a weighed filter, washed, dried at 100° C., and weighed as CdS. In the presence of metals of the fourth group the solution must be slightly acidified with hydrochloric acid and precipitated by a current of sulphuretted hydrogen.

5. ESTIMATION OF COPPER.

(*A*) As Cupric Oxide.

(Practise upon ·5 gramme of pure $CuSO_4 . 5H_2O$.)

The solution is boiled with a slight excess of sodium hydrate. The precipitate is filtered out, washed, and dried. It is then carefully removed from the paper to a weighed crucible, and the filter having been burned on the lid and the ash added to the contents of the crucible, the whole is well ignited, cooled in a desiccator, and weighed rapidly, because cupric oxide is very hygroscopic. To make sure that the oxide contains no cuprous oxide, it is moistened with a little fuming nitric acid, dried with the lid on, ignited for ten minutes, and then weighed as CuO. This operation requires care, being liable to involve loss by spurting.

(*B*) As Metallic Copper.

The solution, which must be free from other metals precipitable by electrolysis, is introduced into a weighed and very clean platinum basin. It must contain a slight excess of sulphuric acid, but on no account nitric acid. The dish is then attached to the wire from the zinc plate of a galvanic cell, thus becoming the *cathode*. The other wire is connected to a piece of platinum wire to form an *anode*, and this latter is then immersed in the liquid. After a short time the fluid will become quite colourless, and the basin will be coated with metallic copper. The fluid is now poured off, and the copper repeatedly washed with boiling water till all acidity is removed. The basin is finally rinsed with absolute alcohol, quickly dried, weighed, and the tare of the basin having been deducted, the difference is metallic copper in the quantity weighed out for analysis.

The use of a battery may be dispensed with, and a fragment of pure zinc used to precipitate the copper, with sufficient acid to dissolve all the zinc before pouring off.

6. ESTIMATION OF BISMUTH.

(*A*) As Bismuth Sulphide.

(Practise upon ·75 gramme of *bismuthi et ammoniæ citras* B.P.)

This process (although employed in the B.P.) cannot be much recommended, as the sulphide is apt to increase in weight on drying, owing to the absorption of oxygen. A current of sulphuretted hydrogen is passed through the acid bismuth solution ; the resulting sulphide is collected on a tared filter, dried at 100° C., and weighed as Bi_2S_3.

(*B*) As Bismuth Oxide.

The solution for analysis is diluted with water, and precipitated with a slight excess of ammonium carbonate. The precipitated bismuthous oxycarbonate is collected, washed, and dried. It is then separated from the filter paper, and the latter having been burned on the lid of a weighed crucible, the whole is introduced into the crucible, and ignited, cooled, and weighed as Bi_2O_3.

7. ESTIMATION OF GOLD.

As Metallic Gold, by Cupellation.

The alloy containing the gold is treated exactly as described under silver. The resulting metallic button is rolled out into a flat foil, and is then digested with nitric acid, which dissolves any silver, and the resulting gold is re-fused into a button and weighed.

8. ESTIMATION OF PLATINUM.

As Metallic Platinum.

The solution, which must contain the platinum as chloride, is concentrated and precipitated with excess of ammonium chloride. The precipitate is well washed with rectified spirit, dried, ignited, and weighed as metallic platinum.

9. ESTIMATION OF TIN.

(*A*) As Stannic Oxide.

Alloys containing tin, but free from antimony or arsenic, are treated with nitric acid, which converts the tin into oxide and other metals into nitrates. The acid fluid is evaporated nearly to dryness, the residue taken up with water and a little nitric acid; the oxide is washed by decantation, collected on a filter, completely washed and dried. It is then as completely as possible detached from the filter, the latter is burned on a lid, the ash added to the contents of the crucible, and the whole ignited. After cooling, the oxide is moistened with a little nitric acid, dried (with the lid on), again ignited, and weighed as SnO_2.

Where we have to deal with tin in solution, the following method is applied:—

The solution, which must be free from other metals of the first three groups, is precipitated with sulphuretted hydrogen, the resulting sulphide is washed with solution of ammonium acetate, which will prevent the stannic sulphide from passing through the filter. The sulphide is transferred to a weighed crucible, and the whole ignited, *at first very gently*, until fumes of sulphurous anhydride cease, and then at a very high temperature, with the addition of a fragment of ammonium carbonate.

This process depends on the conversion of the sulphide into SnO_2 by ignition: but it must be conducted with care, as a too rapid application of heat would cause the change to take place suddenly, and some of the sulphide would be lost.

(*B*) As Metallic Tin.

This process, which is only applicable to tin stone, consists in fusing a known quantity of the pulverised ore with potassium cyanide in a porcelain crucible, when a small button or granules of metallic tin will be obtained on treating the mass with water. The tin is washed, dried, and weighed.

10. ESTIMATION OF ANTIMONY.

As Antimonious Sulphide, with or without Subsequent Conversion into Antimonious Antimonic Oxide.

(Practise upon ·5 gramme of "tartar emetic.")

The acid solution is mixed with tartaric acid, to prevent the precipitation of an oxysalt, diluted with water, and precipitated with sulphuretted hydrogen, the sulphide collected on a weighed filter, dried at 105° C., and weighed. The conversion of the sulphide into oxide is best done by igniting an aliquot part in a porcelain crucible, with excess of mercuric oxide, and finally igniting very strongly. The remaining Sb_2O_4 is then weighed. The B.P. simply moistens and warms the sulphide with nitric acid till red fumes cease, and then dries, ignites, and weighs as Sb_2O_4.

11. ESTIMATION OF ARSENIC.

(*A*) As Arsenious Sulphide.

(Practise upon ·5 gramme As_2O_3.)

The solution must contain the arsenic as arsenious acid. After adding some HCl, a current of sulphuretted hydrogen is passed through the liquid, till the latter acquires a strong smell. The excess of gas is now removed by warming the fluid and passing a current of carbonic anhydride through it. The sulphide is collected on a weighed filter, washed, dried at 100° C., and weighed as As_2S_3.

(*B*) As Magnesium Ammonium Arseniate.

If the substance be arsenious acid it is dissolved in some hot solution of sodium carbonate, excess of hydrochloric acid is added, and the fluid mixed with excess of bromine water. Arsenic and sulphur compounds, on the other hand, are dissolved in hot potassium hydrate and treated with excess of chlorine gas to convert them into arsenic acid. The solution of arsenic acid thus obtained by either of the foregoing methods is mixed with large excess of ammonium hydrate, and, after being allowed to cool, precipitated with *magnesia mixture*. After standing for at least twelve hours, the precipitate is collected on a weighed filter, washed with a mixture of one volume of ammonium hydrate and three volumes of water till free from chlorine, dried for three hours at 105° C., and weighed as $(MgNH_4AsO_4)_2\ H_2O$.

12. ESTIMATION OF COBALT.

As Potassium Cobaltous Nitrite.

The solution is concentrated to a small bulk, the excess of acid is neutralised with potash, and excess of potassium nitrite and a little acetic acid (to keep the solution slightly acid to test-paper) are then added. After the lapse of twenty-four hours all the cobalt will have crystallised out as potassium cobaltous nitrite. This salt is quite insoluble in the mother liquor, but slightly so in pure water. For the washing a 10% solution of potassium acetate is used, wherein the salt is also insoluble, and the acetate is afterwards removed by washing with alcohol. A weighed filter is used and the precipitate dried at 100° C.

13. ESTIMATION OF NICKEL.

As Metal.

The solution is precipitated with excess of sodium hydrate and boiled. The precipitate is washed with boiling water, dried, ignited, and weighed. The ignited residue, or a known portion of it, is now introduced into a weighed porcelain boat, and reduced at red heat by a current of hydrogen. The reduced metallic nickel is afterwards weighed.

14. ESTIMATION OF MANGANESE.

As Manganoso-manganic Oxide.

(Practise upon ·75 gramme of pure $MnSO_4\ .\ 7H_2O$.)

The solution for analysis, if strongly acid, is neutralised with ammonium hydrate and precipitated by ammonium sulphide. The precipitated manganous sulphide is washed with water containing ammonium sulphide, and dissolved in hydrochloric acid. Excess of sodium acetate is then added, and chlorine gas is passed through the liquid until all the manganese precipitates as manganic peroxide, which is then collected, washed, and calcined in a weighed crucible to bright redness. This forms Mn_3O_4; the crucible with the contents is then cooled and weighed.

15. ESTIMATION OF ZINC.

As Zinc Oxide.

(Practise upon ·75 gramme of pure $ZnSO_4 . 7H_2O$.)

The solution of the zinc salt is precipitated, while boiling, with sodium carbonate, and the whole is well boiled. The precipitate is allowed to settle, washed by decantation with boiling water, filtered out, and dried. It is then introduced into a weighed crucible, ignited for some time at a bright red heat, cooled, and weighed. The ignition changes the precipitated zinc carbonate to oxide, and it is weighed as ZnO. Or the solution is precipitated with ammonium sulphide, the zinc sulphide collected on a filter, washed with dilute ammonium sulphide, dried, ignited, and finally weighed as oxide. This latter method is useful when only small quantities of zinc are present.

16. ESTIMATION OF IRON.

As Ferric Oxide.

(Practise upon ·75 gramme of pure $FeSO_4 . 7H_2O$.)

The solution is boiled with a nitro-hydrochloric acid, to ensure that the whole of the iron is in the ferric state. Excess of ammonium hydrate is added, the whole boiled and rapidly filtered. The precipitated ferric hydrate is washed with boiling water, dried, and ignited in a weighed crucible for some time.

In the presence of organic matter, such as citric or tartaric acid, the iron must first be separated by precipitation with ammonium sulphide, the precipitate washed with dilute ammonium sulphide, redissolved in hydrochloric acid, boiled, oxidised by potassium chlorate, and then precipitated with ammonium hydrate, as directed. In the presence of manganese the solution should be nearly neutralised by ammonium hydrate and then boiled with excess of ammonium acetate, and the resulting ferric oxy-acetate collected, washed, dried, and ignited to Fe_2O_3.

17. ESTIMATION OF ALUMINIUM.

As Aluminic Oxide.

(Practise upon 1 gramme of pure alum.)

The solution is precipitated with a slight excess of ammonium hydrate, and boiled until it only smells very faintly of ammonia. The precipitated aluminic hydrate thus obtained is filtered out, washed with boiling water, and dried. The dry filter and its contents are transferred to a weighed platinum crucible, and ignited to bright redness for some time, allowed to cool, and weighed as Al_2O_3.

18. ESTIMATION OF CHROMIUM.

As Chromic Oxide.

Salts of chromium are at once precipitated with ammonium hydrate, and the precipitate washed, dried, ignited, and weighed as Cr_2O_3. Soluble chromates are first reduced by means of hydrochloric and sulphurous acids (or, instead of the latter, spirit of wine may be used), and the chromium precipitated as hydrate by ammonium hydrate, ignited and weighed as Cr_2O_3, all as described above for aluminium.

19. ESTIMATION OF BARIUM.

As Barium Sulphate.

(Practise upon ·5 gramme of $BaCl_2 . 2H_2O$.)

To a solution in boiling water add excess of sulphuric acid, boil rapidly for a few minutes, and set aside to settle.

The clear liquor is poured off as closely as possible, and the precipitate collected on a filter of *Swedish paper*, and washed with boiling water. The filter and precipitate are next dried and ignited in a weighed platinum crucible (the precipitate being removed as perfectly as possible from the paper, and the latter first burned separately on the crucible lid, and the ash added to the contents of the crucible, to avoid the reduction of $BaSO_4$ to BaS by the carbon of the paper). The crucible and its contents having been weighed, and the weight of the crucible and filter ash deducted, the difference equals the $BaSO_4$.

20. ESTIMATION OF CALCIUM.

As Calcium Carbonate.

(Practise upon ·5 gramme of powdered calc-spar dissolved in dilute HCl.)

The solution of the lime salt is mixed with ammonium chloride, and is then made alkaline by ammonium hydrate. Ammonium oxalate is now added in excess. The whole is kept just below the boiling-point until the precipitate aggregates, then filtered and the precipitate washed with hot distilled water until free from chlorides. The filter and contents having been dried at 100° C., the precipitate is carefully transferred to a tared platinum crucible and gently ignited. It is then moistened with a solution of pure ammonium carbonate, evaporated to dryness, heated until no more fumes are evolved, and then weighed as $CaCO_3$.

21. ESTIMATION OF MAGNESIUM.

As Magnesium Pyrophosphate.

(Practise upon ·5 gramme of pure $MgSO_4 . 7H_2O$.)

The solution (which should be strong) is mixed with some ammonium chloride, and then with one-third of its bulk of ammonium hydrate, well cooled, excess of disodium hydrogen phosphate added, and the whole set aside for some hours. Care must be taken not to touch the sides of the beaker with the stirring rod, as otherwise particles of the precipitate will adhere to them so tenaciously as to be only removable with great difficulty. The precipitate is collected on the filter, washed with a mixture of one volume of ammonium hydrate and three volumes of water, till the washings are free from chlorine, and dried. The precipitate is now detached from the filter and put into a weighed platinum crucible, the filter is burned in the lid, the ash added to the contents of the crucible, and the whole strongly ignited and weighed as $Mg_2P_2O_7$.

It sometimes happens that the phosphate, even after prolonged ignition, is very black. In that case it is, after cooling, thoroughly moistened with nitric acid, carefully dried, and re-ignited, when it will be found to be perfectly white.

The B.P. estimates magnesium in $MgSO_4$ by simply precipitating a boiling solution with Na_2CO_3, and collecting, drying, igniting, and weighing as MgO.

22. ESTIMATION OF POTASSIUM.

As Potassium Platino-Chloride.

(To be practised upon ·2 gramme of pure KCl.)

The solution is placed in a small porcelain basin, and mixed with a *good* excess of solution of platinic chloride. The whole is evaporated to dryness on a water bath kept at a temperature of about 94° C. When quite dry it is again digested with a few drops of platinic chloride solution, and taken up with alcohol. The precipitate is collected on a weighed filter, washed with alcohol till the washings appear quite colourless, dried at 100° C., and weighed as $PtCl_4 . 2KCl$.

23. ESTIMATION OF SODIUM.

As Sodium Sulphate.

(Practise upon ·5 gramme of pure NaCl.)

This method is only applicable where we have to deal with a sodium salt containing a volatile acid. The solution is mixed with excess of sulphuric acid and evaporated in a weighed platinum basin. When fumes of sulphuric acid become visible, the basin is covered over with a lid (which has been weighed together with the crucible) and gradually heated till fumes cease. While red hot the lid is lifted up a little, and a small lump of ammonium carbonate put in the crucible, which operation is repeated after a few minutes, and the residual Na_2SO_4 is cooled and weighed. The object of introducing the ammonium carbonate is to remove the last traces of free sulphuric acid.

24. ESTIMATION OF POTASSIUM AND SODIUM IN PRESENCE OF METALS OF FOURTH GROUP.

(Practise upon the residue left on evaporating 1 litre of ordinary drinking-water, and redissolving in a little dilute HCl.)

The solution is first of all precipitated with excess of barium chloride, which throws down sulphuric, phosphoric, etc., acids. Barium hydrate (or some milk of lime) is now added in slight excess, when any magnesia will also be thrown down. To the filtered liquid excess of ammonium carbonate is added, the precipitate is filtered out, and the fluid evaporated to dryness in a platinum crucible on the water bath. When quite dry, it is gently heated as long as white ammoniacal fumes are visible. The residue, which will now consist of alkaline chlorides, is, however, not quite fit for weighing, and must be purified. This is done by redissolving in water, and adding a little ammonium carbonate, when a slight precipitate will form. After filtering, the fluid is evaporated (this time in a tared platinum basin) on the water bath, and when dry the residue is gently heated to faint redness for a minute, cooled, and weighed. When no sodium is present it will now be pure potassium chloride; but should it also contain sodium chloride, it must be redissolved, the potassium estimated by $PtCl_4$, and the sodium obtained by difference. This process is one of the most commonly occurring operations, because it is required in every full analysis of water, and also of the ash of all vegetable and animal substances, where potassium and sodium have always to be estimated in presence of Ca, Mg, phosphates, etc. It is therefore a very important one to thoroughly master.

25. INDIRECT ESTIMATION OF POTASSIUM AND SODIUM.

The weighed mixture of KCl + NaCl obtained as in 24 is redissolved in distilled water and titrated with $\frac{N}{10}$ solution of argentic nitrate (see p. 116). The number of c.c. having been noted and multiplied by ·003519, we obtain the amount of Cl present in the mixed chlorides. If now all this Cl had been present as KCl, every 35·19 Cl would represent 74·02 KCl, but if present as NaCl, then 35·19 Cl would equal 58·07 NaCl, thus showing a theoretical difference of 15·95, which we will call *d*. We therefore first calculate:—

$$\frac{74{\cdot}02 \times \text{Cl found}}{35{\cdot}19} = x \text{ grammes, if all KCl.}$$

From this we deduct the actual weight of the mixed chlorides found, and obtain a practical difference, which we will call *d′*. Then: –

$$\frac{d' \times 58{\cdot}07}{d} = \text{the weight of NaCl present in the mixed chlorides.}$$

and by deducting this from the total mixed chlorides the balance is KCl.

26. ESTIMATION OF AMMONIUM.

As Ammonium Platino-Chloride.

If the solution contains other basylous radicals, a known quantity of it is distilled with some slaked lime in a suitable apparatus, and the distillate received into dilute hydrochloric acid. About three-fourths is distilled over. The distillate is then evaporated to dryness with excess of pure platinic chloride (free from nitro-hydrochloric acid). The dry residue is now treated with a mixture of two volumes of absolute alcohol and one of ether, collected on a weighed filter, washed with the said ether mixture, dried at 100° C., and weighed as $PtCl_4 . 2NH_4Cl$.

A less expensive method is to distil the ammonia into a known bulk of volumetric acid, and then check back with volumetric soda, so finding the amount of acid neutralised by the ammonia.

DIVISION III. GRAVIMETRIC ESTIMATION OF ACID RADICALS.

1. ESTIMATION OF CHLORIDES.

As Argentic Chloride.

(Practise upon ·5 gramme pure NaCl.)

The solution containing the chloride is precipitated with argentic nitrate. Nitric acid is then added, and the whole stirred till the liquid is perfectly clear. The precipitate is now treated as directed (see Silver, p. 142). After weighing the chloride it is calculated to Cl.

2. ESTIMATION OF IODIDES.

3. ESTIMATION OF BROMIDES.

4. ESTIMATION OF CYANIDES.

The process for each of these is practically the same as for chloride. The argentic cyanide is, however, collected and weighed upon a weighed filter. The argentic iodide and bromide are treated like the chloride; but *if* a filter is used, it must be a weighed one. The filter is afterwards reweighed, and the increase in weight is the amount of argentic iodide or bromide carried on to the filter during the washing by decantation.

5. ESTIMATION OF AN IODIDE IN THE PRESENCE OF A CHLORIDE AND A BROMIDE.

By Palladium.

The solution, slightly acidified, is precipitated with excess of palladious chloride. The whole is then allowed to stand in a warm place for twenty-four hours, so that the precipitate may thoroughly settle. The supernatant liquor is poured off, and the precipitate having been collected on a filter, and washed, is placed in a weighed platinum crucible and ignited. The whole is then again weighed, and the weight, less that of the crucible and filter ash, equals the amount of metallic palladium left after ignition, which × 2·396 = the amount of iodine in the weight of the sample taken for analysis.

Note.—A method for estimating chloride in the presence of bromide will be found on page 116.

6. ESTIMATION OF SULPHIDES.

By Conversion into Sulphate.

(Practise upon ·5 gramme of purified "black antimony.")

Fuse with a large excess of a mixture of potassium nitrate and carbonate, extract the fused mass with water, filter, acidulate with hydrochloric acid, add excess of barium chloride, and proceed as for a sulphate; but calculate at the last to sulphur instead of sulphuric acid. Some sulphides can be attacked by dissolving in nitric acid with the addition of successive small crystals of potassium chlorate. Excess of hydrochloric acid is added, and the whole having been evaporated to dryness, the residue is then boiled with dilute hydrochloric acid, filtered, and the filtrate precipitated with barium chloride.

7. ESTIMATION OF SULPHATES.

As Barium Sulphate.

(Practise upon ·5 gramme of $MgSO_4 . 7H_2O$.)

The solution is acidulated with hydrochloric acid, excess of barium chloride is added, and the whole boiled. When quite clear a little more barium chloride is added, to ascertain whether all the sulphate has precipitated. The precipitate is now treated precisely as in the barium estimation (page 149) and the resulting $BaSO_4$ is calculated to sulphate.

8. ESTIMATION OF NITRATES.

(*A*) In Alkaline Nitrates.

If nitric acid be required to be estimated in, say, ordinary nitre, the sample must first be heated to fusion to remove moisture, and then be quickly powdered. A weighed quantity of it is now mixed in a platinum crucible with (exactly) four times its weight of plumbic sulphate. The mixture is ignited till it ceases to lose weight, when the loss will just represent the amount of nitric anhydride in the sample taken for analysis.

The reaction is represented by the following equation:—

$$PbSO_4 + 2KNO_3 = PbO + K_2SO_4 + 2NO_2 + O.$$

(*B*) By Conversion into Nitric Oxide.

Already described at page 133.

(*C*) By Conversion into Ammonia.

The nitrate is converted into ammonia by the action of nascent hydrogen, thus:—

$$HNO_3 + 4H_2 = NH_3 + 3H_2O.$$

The nascent hydrogen may be applied in various ways, as follows:—

1. By distillation with sodium hydrate and metallic aluminium, and receiving the evolved ammonia into a known volume of normal standard acid.
2. By acting on the nitrate for 12 hours with zinc or iron and dilute sulphuric acid, and then adding excess of sodium hydrate, and distilling off the ammonia into a known volume of normal standard acid.

The standard acid used is then titrated by normal standard sodium hydrate, and the excess of acid started with, over that of alkali now used, gives the number of c.c. of standard acid neutralised by the ammonia. This number multiplied by ·06258 = HNO_3 present, or by ·05364 = N_2O_5.

9. ESTIMATION OF PHOSPHATES.

(*A*) Estimation of the Strength of Free Phosphoric Acid.

1 gramme of the acid is evaporated in a weighed dish with 2·5 grammes of PbO; the dry residue is ignited and its weight noted. Thus treated, strong B.P. acid should yield 2·98 grammes and the diluted acid ·6 gramme of residue.

(*B*) As Magnesium Pyrophosphate in Alkaline Phosphates.

(Practise upon ·75 gramme of pure $Na_2HPO_4 . 12H_2O$.)

Ammonium hydrate and *magnesia mixture* are added in excess, and the precipitate is treated as directed under Magnesium (page 149). Should the solution contain meta- or pyro-phosphates it must either be previously boiled with strong nitric acid for one hour, or be fused with potassium sodium carbonate.

(*C*) As Magnesium Pyrophosphate in the Presence of Calcium and Magnesium.

(Practise upon ·5 gramme of pure $Ca_3(PO_4)_2$ dissolved in dilute HCl.)

The solution (which must contain orthophosphoric acid, or, failing that, should be boiled with HNO_3 as above) is precipitated with ammonium hydrate, and the precipitate is redissolved in the smallest amount of acetic acid. The calcium is then removed by adding excess of ammonium oxalate, and the filtrate having been evaporated to a bulk not exceeding 3 ounces is cooled, treated with excess of ammonium hydrate and *magnesia mixture*, and the precipitate is collected as already described for magnesium (page 149). This process is suitable for determining the "*soluble phosphates*" in an artificial manure.

(*D*) As Magnesium Pyrophosphate in the Presence of Iron and Aluminium.

(Practise upon ·75 gramme of B.P. *Ferri phosphas* dissolved in dilute HCl.)

The solution is mixed with excess of ammonium acetate, boiled, and ferric chloride added till a dark-brown precipitate forms. This is washed with boiling water and redissolved in a small quantity of dilute HCl. About five grammes (or more) of citric acid are now introduced, and ammonium hydrate is added to the whole in large excess, and, after cooling, *magnesia mixture*, the precipitate being treated as for magnesium. If the addition of excess of NH_4HO does not produce a clear lemon-yellow solution, then enough citric acid has not been added.

(*E*) Estimation as Phosphomolybdate.

If necessary, the acid solution is heated and precipitated with H_2S to remove arsenic. The excess of H_2S is boiled off, and large excess of nitric acid is added. An excess of ammonium molybdate and ammonium nitrate dissolved in nitric acid is now poured in,[*] the liquid boiled, and finally allowed to stand for some hours in a warm place. The precipitate is filtered off, washed with dilute alcohol until free from acidity, redissolved in dilute ammonium hydrate, the solution evaporated in a weighed dish on the water bath and the residue dried in the water oven. Its weight ÷ 28·5 $= P_2O_5$ present. This process is the best for determining small amounts of total phosphates in cast iron, waters, and soils.

10. ESTIMATION OF TOTAL AND SOLUBLE PHOSPHATES IN AN ARTIFICIAL MANURE OR OF TOTAL ONLY IN SOIL.

(*A*) Total Phosphates.

About 2 grammes of the finely powdered substance are weighed accurately, transferred to a beaker and decomposed with HCl, and where necessary with the addition of a drop or two of HNO_3. The solution is then evaporated to dryness in a water bath, taken up with HCl, and after digestion the insoluble silicious matter is separated by filtration; a weighed quantity of citric acid is added, the solution heated up nearly to boiling point, and a weighed quantity of ammonium oxalate added. The quantities used must vary with the substance under examination, the knowledge only being acquired by experience; but it is seldom necessary to add more than 2 grammes citric acid or 2·5 grammes ammonium oxalate. The free acid is then just neutralised with dilute ammonia, and acetic acid added, to decidedly acid reaction. The liquid is kept simmering for a few minutes with constant stirring, and after standing a short time the calcium oxalate is filtered out. Great care must be observed not to have too large an excess of ammonium oxalate present, as magnesium oxalate in an ammoniacal solution is somewhat easily precipitated. To the filtrate ammonia of ·880 sp. gr. is added to about one-fourth of the bulk; and to the liquid, which must remain clear, or only slowly throw down a small precipitate, due to the magnesia present, *magnesia mixture* is added in moderate excess. The liquid must be set aside, with occasional stirring for the precipitate to form—the time required being principally determined by the quantity of alumina present. It is best, however, to allow it to stand over night, although in cases where the alumina is absent, or small, the precipitation will be found to be complete in two hours. The precipitate is then separated from the liquid by filtration, dissolved in as little HCl as possible, and reprecipitated with one-third of its bulk of ammonia. After allowing to stand for two hours with occasional stirring, it may be filtered, and after drying converted, by ignition in a weighed platinum crucible, into $Mg_2P_2O_7$, and weighed as such.

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[*] This solution is prepared by dissolving 10 grammes of molybdic acid in 41·7 c.c. of ammonia solution ·960 sp. gr., and then adding to 125 c.c. of nitric acid, sp. gr. 1·20.

The calcium oxalate is converted into $CaCO_3$ by gentle ignition, weighed, dissolved in HCl, and tested for P_2O_5, which may be present in small quantities, and if so it should be determined.

The $Mg_2P_2O_7$ is calculated to $Ca_3(PO_4)_2$ unless a full analysis is being made, when it is calculated to P_2O_5, and divided *pro rata* among the bases actually found to be in combination with it.

Note.—Recent researches have shown that by the addition of a sufficiently large amount of citric acid, all the intermediate steps of the process are saved, it being only necessary to afterwards add the excess of ammonia and *magnesia mixture*. By this method, a large excess of citric acid having been first introduced, ammonia is added, and should no precipitate occur, it is followed by the *magnesia mixture*; but if even a cloud should appear, more citric acid must go in, until sufficient has been added to cause a perfectly clear solution on the subsequent addition of ammonia. The whole must stand in the cold for at least twenty-four hours before filtering off the precipitate of ammonium magnesium phosphate, so that, after all, no time is saved by the new method, but the risk of loss is less, because the intermediate filtration (to remove calcium) is avoided.

(*B*) Soluble Phosphates.

Five grammes of the manure are well triturated in a mortar with distilled water, washed into a stoppered 250 c.c. flask, and made up to the mark with water. After standing with occasional shaking for two hours, 100 c.c. (= 2 grammes of sample) is drawn off by a pipette into a beaker, 2 grammes of citric acid and 2·5 grammes of ammonium oxalate are dissolved in the liquid, which is then treated with ammonia, acetic acid, etc., as above described. If the amount of soluble calcium comes out low, the process should be repeated, using such a weighed quantity of ammonium oxalate as will just remove it from solution. This is because the great source of error in phosphate estimations is the use of excess of oxalate, causing the precipitation of magnesium oxalate with the magnesium ammonium phosphate. The adoption of the direct citric acid and ammonia method (given above) of course avoids any difficulty in this respect. The $Mg_2P_2O_7$ is calculated to $Ca_3(PO_4)_2$, and reported as "phosphate made soluble."

11. ESTIMATION OF ARSENIATES.

Arseniates are estimated precisely like phosphates; but the precipitate of ammonium magnesium arseniate is dried at 105° C. on a weighed filter, as already directed under Arsenic. The precipitate thus dried is $(MgNH_4AsO_4)_2 . H_2O$; or, for simplicity of calculation, $MgNH_4AsO_4 . \frac{1}{2}H_2O$.

12. ESTIMATION OF CARBONATES.

A carbonate is estimated by the loss of weight it undergoes by the displacement of its carbonic anhydride by an acid. A small and light flask is procured and fitted with a cork through which passes a tube (c) containing fragments of calcium chloride (see fig. 35). A weighed quantity of the carbonate is introduced into the flask with a little water, and a small test-tube about two inches long is filled with sulphuric acid and dropped into the flask, so that, being supported in an upright position, none of the acid shall mix with the carbonate. The cork is put in, and the weight of the whole apparatus having been carefully noted, it is inclined so as to allow the acid to run from the small tube into the body of the flask. Effervescence sets in, the carbonate is dissolved, and the CO_2, escaping through the calcium chloride tube, is deprived of any moisture it might carry with it. When all action has ceased, and the whole has cooled, air is drawn through the apparatus to displace the remaining CO_2 and it is once more weighed. The difference between the two weights gives the amount of CO_2 evolved.

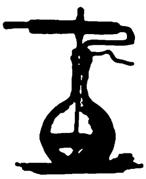


Fig. 35.

A better apparatus is that figured (No. 36), in which C is the flask, A the tube to contain HCl to decompose the carbonate, and B a tube containing strong H_2SO_4, through which the evolved CO_2 must pass, and so be perfectly deprived of moisture.

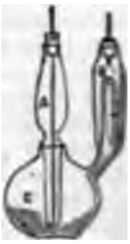


Fig. 36

13. ESTIMATION OF BORIC ACID IN BORATES.

This is best done by distilling off the boron in the form of methyl borate, and finally estimating it as calcium borate. The apparatus required is a distilling flask heated by a water-bath and fitted with a tap-funnel, the tube of which reaches nearly to the bottom of the flask. The side delivery-tube is attached to an upright condenser having a spiral worm and ending in a receiver standing in a dish of cold water and furnished with a set of bulbs containing dilute ammonia, to ensure against the escape of any methyl borate.

The weighed quantity of the boric acid (or borate) is put into the flask with as little liquid as possible, and 1 c.c. of nitric acid having been added, the whole is distilled to dryness. 10 c.c. of methyl alcohol are then introduced by the funnel and entirely distilled off, which operation is repeated four times. 2 c.c. of an equal mixture of nitric acid and water are again added, distilled off, and the treatment with methyl alcohol is continued until a drop of the distillate, absorbed into filter-paper, ceases to burn with a green flame. While this distillation is proceeding, some pure lime (10 grammes for every ·5 gramme of borate taken) is put into a platinum dish, heated for some time over the blow-pipe, cooled under the desiccator and weighed. The weighed dish and lime having been placed on ice, the contents of the receiver and bulbs are added to it and, after standing for twenty minutes, the whole is very cautiously evaporated at a temperature below 59° C. The heat is then gradually increased until the mass is quite dry and the whole is finally ignited over the blow-pipe and weighed. The increase in weight is the B_2O_3 from the weight of sample started with.

14. ESTIMATION OF OXALIC ACID.

As Calcium Carbonate.

The solution is made alkaline with ammonium hydrate and precipitated with calcium chloride. The precipitate is washed till free from *chlorides*, dried, ignited, and finally weighed as carbonate, as directed under Calcium (page 149).

15 ESTIMATION OF TARTARIC ACID.

As Calcium Oxide.

The solution (which must contain no other bases than K, Na, or NH_4) is made *faintly* alkaline by sodium hydrate, and precipitated by excess of calcic chloride. The precipitate is washed with cold water, dried, ignited (with the blowpipe), and weighed as calcic oxide.

16. ESTIMATION OF SILICIC ACID.

(*A*) In Soluble Silicates.

By soluble silicates are meant those which are either soluble in water of in hydrochloric acid. The solution (which must contain some free HCl) is evaporated to dryness on the water bath, and the residue dried for an hour at 120° C. (248° F.). After cooling, the mass is moistened with strong hydrochloric acid, and then boiled with water, thus leaving an insoluble residue of pure silica—SiO_2—which is collected on a filter, washed, dried, ignited, and weighed.

(*B*) In Insoluble Silicates.

These bodies must be decomposed by mixing a weighed quantity of the finely powdered substance with four times its weight of sodium potassium carbonate, and fusing the whole for about half an hour. (*When alkalies have to be estimated, a separate special fusion must be made with barium hydrate, or pure lime mixed with ammonium chloride, instead of the double carbonate.*) The crucible must be well covered during fusion. After cooling, the residue is treated with dilute and warm HCl until effervescence ceases, evaporated to dryness, and treated as above described at 120° C. (248° F.), etc.

DIVISION IV. GRAVIMETRIC SEPARATIONS.

This department is beyond the scope of the present edition. When the student has practised all the contents of the book up to this point, he will already have a sufficiently general idea of chemical analysis to enable him to fix the line of work he desires to make his speciality. If this be mineral analysis, he must pass to a larger book, such as "Fresenius," to complete his knowledge. So as to give, however, some idea of how the preceding processes may be joined in performing the full analysis of a mixture, we take the following example, because it is a standard one, and give a sketch of the manner of working in performing :—

The Full Analysis of the Mineral Contents of a Sample of Ordinary Potable Water.

Step I. Take the total solid residue of 100 c.c. (calculated in grains per gallon) as directed in Chapter X., to serve as a check on the results; then ignite and again weigh : loss = *organic and volatile matter*.

Step II. Evaporate 2000 c.c. of the water to dryness in a large porcelain dish. Moisten the residue with 10 c.c. of distilled water, and then add 200 c.c. of dilute alcohol ·92 sp. gr. : having gently detached it all from the dish, filter and wash with similarly diluted alcohol till practically nothing more dissolves. This procedure is useful because it separates the salts present thus :—

(*a*) The filtrate may contain all salts of K and Na, chlorides and nitrates of Ca and Mg, and the sulphate of Mg.

(*b*) The insoluble residue may contain the sulphate and carbonate of Ca and the carbonate of Mg, together with any iron and silicious matter present.

(1) *Analysis of the filtrate.*

(*a*) Evaporate till the spirit is driven off, cool, transfer to a 200 c.c. flask, and make up to the mark with distilled water. Divide into two portions of 100 c.c. respectively, marking them A and B.

(*b*) To A add NH_4Cl, NH_4HO and $(NH_4)_2C_2O_4$, to precipitate the Ca, and estimate as usual as $CaCO_3$. Calculate to CaO, and then × 2 = CaO present as Cl or NO_3, in the original 2000 c.c. of water taken.

(*c*) To filtrate and washings from (*b*), concentrated to 50 c.c. and cooled, add Na_2HPO_4, to precipitate Mg, treat as usual, and weigh as $Mg_2P_2O_7$. Calculate to MgO, and then × 2 = MgO present as Cl, SO_4 or NO_3 in the original 2000 c.c. of water.

(*d*) To B acidulate with HCl and add $BaCl_2$ to precipitate sulphate. Treat as usual and weigh as $BaSO_4$. Calculate to SO_3, and then × 2 = total SO_3 present in the original 2000 c.c. of water taken in combination with K or Na.

(*e*) The filtrate and washings from (*d*) are evaporated to a low bulk rendered alkaline with pure $Ca(HO)_2$, the separation for alkalies given at page 150 gone through, and the K and Na present both estimated as chlorides. Results × 2 = total K and Na present in the 2000 c.c. of water started with.

(*f*) The residue from (*e*) is dissolved in a little water, and the K estimated thereon by $PtCl_4$ in the usual manner and calculated to K_2O (see page 150). An equivalent amount of KCl (calculated from this K_2O) is then deducted from residue (*e*), and the balance is NaCl, which is calculated to Na_2O.

(2) *Analysis of the insoluble portion.*

(*a*) This is washed from the filter with distilled water and then boiled with 100 c.c. of H_2O and HCl added till effervescence ceases. Any insoluble is filtered out, washed with boiling H_2O, dried, ignited, and weighed = *silicious matter* in the 2000 c.c. of water started with.

(*b*) The filtrate and washings are warmed with a drop or two of HNO_3 and mixed with $NH_4Cl + NH_4HO$, and the iron estimated if present as Fe_2O_3, and result calculated to Fe = total Fe in the 2000 c.c. of water taken.

(*c*) Divide filtrate and washings into two equal parts, A and B.

(*d*) The portion A is precipitated with $(NH_4)_2C_2O_4$, and the calcium estimated as $CaCO_3$ and calculated to CaO. Result × 2 = total CaO as carbonate or sulphate in the original 2000 c.c. of water taken.

(*e*) The filtrate from (*d*) is concentrated to a low bulk, cooled, and Na_2HPO_4 added with excess of NH_4HO, and the Mg estimated as usual as $Mg_2P_2O_7$, and calculated to MgO. Result × 2 = total MgO present as carbonate in the original 2000 c.c. of water.

(*f*) The portion B is acidulated with HCl, and the sulphate estimated by $BaCl_2$, weighed as $BaSO_4$, and calculated to SO_3. Result × 2 = total SO_3 in combination with Ca in the original 2000 c.c. of water.

Step III. Evaporate 250 c.c. of the water to a bulk of 2 c.c., and treat in the nitrometer to estimate the nitric acid (see page 134). Resulting NO calculated to N_2O_5 and × 8 = total N_2O_5 present in 2000 c.c. of water.

Step IV. Take the amount of chlorides volumetrically (page 116) in 100 c.c. of the water. Result × 20 = Cl in 2000 c.c. of water.

Step V. *Calculation of results.*

(*a*) All our results being in grammes or fractions of the same from 2000 c.c. of water, each must be multiplied by 35, which will bring them all to grains per imperial gallon (parts in 70,000). The analysis is then stated as follows (example taken from actual practice):—

A sample of water yielding 20·1 grains of total solids per gallon, of which ·45 grain was "organic and volatile matter," and the balance (19·65 grains) was mineral matter, showed on analysis:—

(*a*) In the portion soluble in spirit:

	grains per gallon.
Potassium oxide . . .	·2704
Sodium oxide . . .	1·4097
Chlorine	1·2133
Sulphuric anhydride .	·6803
Calcium oxide . . .	none.
Magnesium oxide . . .	none
Nitric anhydride . . .	none.

(*b*) In the portion insoluble in spirit:

	grains per gallon.
Calcium oxide . . .	7·3953
Magnesium oxide . . .	1·0000
Sulphuric anhydride . .	1·7647
Silicious matter . . .	·2000
Ferric oxide . . .	·0500
Total found . .	13·9837

From this residue is now to be always deducted an amount of oxygen equivalent to the chlorine found, because all the bases have been calculated to oxides, while haloid salts contain no oxygen. The chlorine found is 1·2133, and—

$$\frac{1·2133 \times 16}{71} = ·2737 \text{ oxygen, equivalent to Cl found.}$$

Performing the deduction, we have—

$$13·9837 - ·2737 = 13·7100 \text{ grains of solid matter actually found.}$$

The total residue, after driving off organic matter, was 19·65 grains per gallon, and the difference is due to CO_2 unestimated, thus

$$19·65 - 13·71 = 5·94 \text{ grains of } CO_2 \text{ per gallon.}$$

Adding now this CO_2 to the substances actually estimated, we get—

$$\text{Total substances found} + CO_2 = 19·65,$$
$$\text{Actual residue found} = 19·65,$$

which proves our analysis to be correct.

It now remains to calculate how these bases and acids are probably combined as salts actually present, by the following general rules of affinity, thus:—

(*a*) *In the portion soluble in spirit.* (1) Any sulphuric anhydride will prefer the bases in the following order: K, Na, Mg. (2) Chlorine will prefer the bases in the same order *after the SO_3 is satisfied.* Therefore we first calculate our K_2O to K_2SO_4, which gives ·50 and uses up ·2296 of our SO_3, and the balance of SO_3 (·4507) we calculate to Na_2SO_4. This gives ·80 Na_2SO_4, and leaves 1·0604 Na_2O not as sulphate and therefore existing as chloride.

Calculating accordingly, we get 2·00 of NaCl, which just uses up all our chlorine. Therefore this portion contained altogether—

Potassium sulphate	·50
Sodium sulphate	·80
Sodium chloride	2·00

(*b*) *In the portion insoluble in spirit.* (1) The SO_3 found will all be present as $CaSO_4$, and the balance of CaO and all the MgO will be as carbonates. Therefore 1·7647 SO_3 calculated to $CaSO_4$ becomes 3·00 and uses up 1·2353 of CaO, leaving 6·16 to be calculated to $CaCO_3$. This yields 11·00 $CaCO_3$, and the 1·00 of MgO found, calculated to $MgCO_3$ gives 2·10. Thus this portion contains—

Calcium sulphate	3·00
Calcium carbonate	11·00
Magnesium carbonate	2·10

Putting now the whole analysis together, we have—

Potassium sulphate	·50
Sodium sulphate	·80
Sodium chloride	2·00
Calcium sulphate	3·00
Calcium carbonate	11·00
Magnesium carbonate	2·10
Ferric oxide	·05
Silica	·20
Organic and volatile matter	·45
Total residue	20·10

CHAPTER IX.

ULTIMATE ORGANIC ANALYSIS.

THIS process consists in estimating the amount of each element present in any organic compound, as distinguished from proximate analysis, which estimates the amounts of the compounds themselves.

I. LIST OF APPARATUS REQUIRED.

1. A combustion furnace, which is a series of Bunsen burners arranged in a frame so as to gradually raise a tube placed over them to a red heat. The tube lies in a bed made of a series of firebricks, which confine the heat and make it play all round the tube (see fig. 37).
2. Combustion tubes made of hard glass, not softening at a red heat. These tubes are closed at one end by drawing out before the blowpipe and turning up. The mode of doing this is illustrated in fig. 38.

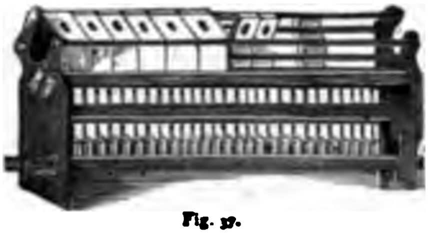


Fig. 37.

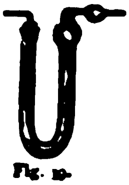


Fig. 39.

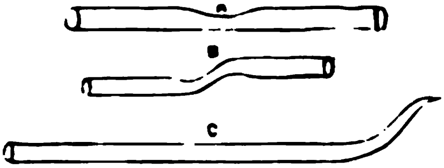


Fig. 38.

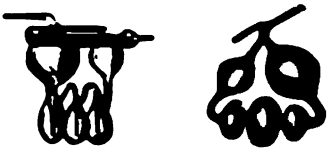


Fig. 40.

3. U tubes packed with perfectly dry calcium chloride in small fragments, so as to allow the free passage of gases (illustrated in fig. 39), and hereafter referred to for brevity as "$CaCl_2$ tubes."
4. Bulbs charged with strong solution of potassium hydrate (1 in 1), hereafter for brevity referred to as "KHO bulbs." Two common forms of such bulbs are illustrated in fig. 40.
5. Bulbs for absorbing ammonia and intended to be charged with dilute acid of known strength, and hereafter referred to as "nitrogen bulbs" for brevity. Two common forms of such bulbs are illustrated in fig. 41.
6. Graduated tubes closed at one end, to hold 50 c.c., and graduated from the closed end downwards in $\frac{1}{10}$ of a c.c., used for collecting gases and measuring them after collection, hereafter referred to as "gas-collecting tubes" for brevity. fig. 42.
7. A deep cylindrical vessel of glass filled with water and furnished with a thermometer dipping in the water, the whole sufficiently deep to permit of the entire immersion of the gas-measuring tubes, and wide enough at the top to admit the hand, as shown in fig. 43. This is hereafter called the "measuring trough" for brevity.

8 Glass towers, filled in one limb with fragments of $CaCl_2$ to absorb moisture, and in the other with fragments of soda-lime to absorb carbon dioxide. These are illustrated in fig. 44, and are used for freeing any air which may be caused to pass through them from moisture and CO_2; hereafter called "air-purifying towers" for brevity.

II. ESTIMATION OF CARBON AND HYDROGEN.

I. **Liebig's Process.**—This process is performed by heating a weighed quantity of the substance in a tube with some body readily parting with oxygen at a red heat, such as cupric oxide or plumbic chromate, by which the hydrogen and carbon of the organic body are respectively oxidised into water and carbonic anhydride. These products are passed first through a weighed tube containing calcium chloride, which retains the water, and then through a weighed bulb apparatus containing potassium hydrate, which absorbs the carbonic anhydride. After the experiment is finished, the increase in weight of the tubes is calculated thus:

As $H_2O : H_2 : :$ increase in $CaCl_2$ tube : x.
As $CO_2 : C : :$ increase in KHO bulbs : x.

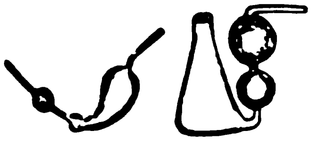


Fig. 41.

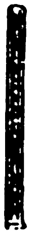


Fig. 40.

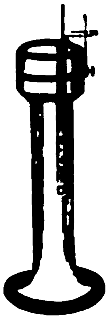


Fig. 43.

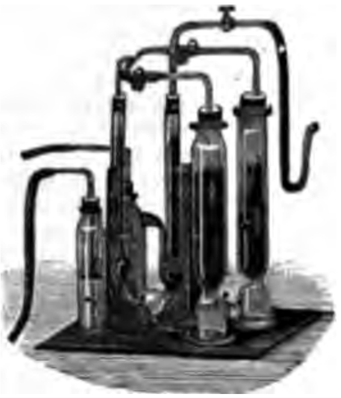


Fig. 44.

The details of the actual process are as follows:—

(1) *Preliminary steps.*

(*a*) Choose a combustion tube, drawn out and sealed at one end (fig. 38), about eighteen inches long and ½ to ⅝ inch in bore, and fit two corks to it, one whole and the other bored so as to be all ready to take the bulb end of the $CaCl_2$ tube (fig. 39), which must fit air-tight when pushed through the cork.

(*b*) Measure out sufficient CuO (powdered) to fill the combustion tube, and put it into a small pear-shaped hard glass flask over a good "Bunsen" to heat to dull redness and drive off all moisture. Then remove the source of heat, cork it up, and let it cool.

(*c*) While the CuO is cooling weigh your $CaCl_2$ tube and your KHO bulbs (fig. 40), and, having noted their respective weights, close the open ends by means of short pieces of black rubber tubing, having bits of glass rod put in to act as stoppers.

(*d*) ·4 gramme of $KClO_3$ is then to be weighed out, powdered and heated *gently* in a porcelain capsule until it *just* fuses. The fused mass is crushed to powder by a glass rod and the capsule put under the desiccator.

(*e*) ·3 to ·4 gramme of the substance is (if solid) weighed on a watch-glass and put under the desiccator. If liquid, a very minute stoppered tube (to be obtained at any apparatus shop) is weighed, and having been filled with the liquid it is closed and again weighed, the difference being the weight of liquid taken.

(*f*) Sufficient asbestos fibre to make a plug that will occupy about ½ inch of the combustion tube is heated to redness and cooled under the desiccator.

(*g*) A long wire with a curled end is got ready.

(2) *Charging the combustion tube.* When the CuO has cooled sufficiently so that it can be handled, the $KClO_3$ is first dropped into the combustion tube and is followed by four inches of CuO (rapidly transferred from the flask with as little exposure to the air as possible). The weighed substance, if solid, is then dropped in, and immediately followed by another three inches of CuO. The long wire is then used to mix the substance through the upper six inches of CuO, taking care not to disturb the lower inch or the $KClO_3$ (if a liquid only two inches of CuO are put in, and then the bottle is dropped in and followed by five inches of CuO). The tube is now filled with CuO to within two and a half inches of its end; the asbestos is introduced so as to form a loose plug, leaving a space of an inch between it and the charge, and the tube is securely corked. It is then laid flat upon the table and tapped thereon until its contents settle down, so leaving a clear passage for any gases along the upper part of the tube, which is then placed in the furnace (fig. 37) with the corked end just protruding. The cork is removed and the $CaCl_2$ tube is attached by means of the perforated cork (taking care to put the "bulbed" limb next the tube), and to the other end of that the KHO bulbs are attached by means of a piece of black rubber tubing, seeing that the larger side of the bulbs is next the $CaCl_2$ tube. The whole apparatus is now complete, and after testing it for air tightness of the cork and joints (by gently warming the inner side of the KHO bulbs so as to expel some of the air, and seeing that on cooling the liquid stands at a higher level in the inner bulb than before), we are ready to perform:—

(3) *The Combustion.* We first light the first six burners next the bulbs, and when the front part of the tube is red-hot we carefully light the other burners one at a time, so as to cause the heat to travel gradually backwards. The art is to so regulate our heat as never to produce bubbles of gas passing through the bulbs at a more rapid rate than can be distinctly counted. When the whole tube is red-hot, all except the last inch, and the evolution of gas has practically ceased, we light the last burner and cause an evolution of oxygen from the $KClO_3$ which clears the tube of any residual gases and carries them through the bulbs. The gas is then turned off, and when cooled the $CaCl_2$ tube and KHO bulbs are detached and reweighed, and the increase noted in each case.

(4) *Calculation of results.* The following is an example of the method of calculating; the substance under analysis being sugar-candy.

Weight of sugar taken	·475	gramme.
Potash bulbs after combustion weighed . . .	70·113	grammes.
„ „ before „ „ . . .	69·382	„
Difference, due to CO_2 . . .	·731	„
Calcium chloride tube after combustion weighed .	23·405	grammes.
„ „ before „ „ .	23·130	„
Difference, due to H_2O . . .	·275	„

$\frac{(C)\ 12 \times \cdot 731}{(CO_2)\ 44} = \cdot 1994$ carbon. $\frac{(H_2)\ 2 \times \cdot 275}{(H_2O)\ 18} = \cdot 03056$ hydrogen.

Total sugar taken	·475	
Total C and H found	·22996	
Difference, due to oxygen . .	·24504	
Or, in percentage—Carbon		41·98
Hydrogen		6·43
Oxygen		51·59
		100·00

Special Notes to the Foregoing Process.

(*a*) Substances containing sulphur, phosphorus, arsenic, chlorine, or any halogen, are best mixed with fused and powdered plumbic chromate instead of cupric oxide, so as to avoid the formation of volatile cupric compounds.

(*b*) When the substance also contains nitrogen, the front part of the combustion-tube must be plugged with a roll of bright copper gauze about four inches long instead of the asbestos. This is to reduce any oxide of nitrogen, which if allowed to pass into the potash would be absorbed and count as carbon dioxide. The copper, however, takes the oxygen, and only leaves nitrogen, which passes unabsorbed.

(*c*) Very refractory bodies, such as coal, starch, etc., are best burned with plumbic chromate, or should be done by the improved process, in a current of air or of oxygen, to be next considered.

II. The Improved Modern Process.—The difficulty of Liebig's method lies in the hygroscopic nature of CuO, which is so marked that it is scarcely possible to transfer it from the drying flask to the tube without getting some moisture, thus, of course, vitiating the hydrogen determination, to avoid which we proceed as follows:—

A combustion tube, about twenty inches long and open at each end, is charged as shown.

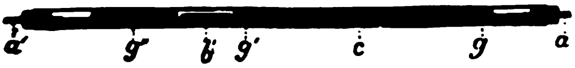


Fig. 44A.—*a* is the front end, to which the $CaCl_2$ tube and KHO bulbs are attached; *a'* is the back end, to which a set of "air-purifying towers" (fig. 44) are attached; *c* is a layer of *granulated* CuO, twelve inches long; *g* and *g'* are small rolls of copper gauze, about half an inch long, to keep the CuO in its place; *b* is a platinum boat to contain the weighed substance, either solid or in a little tube as already described; *g"* is a roll of *oxidised* copper gauze, three and a half inches long.

If the body also contains *nitrogen*, the roll *g* must be made of *bright* copper gauze, four inches long, thus nearly filling the empty space shown. To perform the process the tube is placed in the furnace, and *a'* having been connected to the "towers," they are in turn attached to a gasometer containing air or oxygen. The roll *g"* and the boat *b* having been withdrawn the layer of CuO is heated to redness, and a slow, steady stream of air or oxygen is passed from the gasometer. When the CuO is quite dry the air is stopped, the heat is reduced, the weighed tube and bulbs are attached to *a*, and the cork *a'* having been opened, the boat and roll are replaced, and the whole again closed up, and the air gently turned on. The CuO having again been raised to a redness, the burner under the boat is lighted, and the heat cautiously applied, so as to gradually burn the substance entirely away. At the end of the process the air is stopped, and the $CaCl_2$ tube and KHO bulbs detached and weighed. Any number of combustions can be done one after another by simply re-oxidising the reduced CuO, by heating and turning on the air for a few minutes, and then proceeding again as before. This is the really practical method, and many analysts prefer to suck the air through, by means of an aspirator attached to the outer end of the KHO bulbs, instead of driving it from a gasometer. In using oxygen it is, however, always driven from one of the steel tubes in which it is sold in the compressed state.

III. ESTIMATION OF NITROGEN.

The **estimation of nitrogen** in all compounds, not being nitrites or nitrates, is conducted as follows:—

I. **The Method of Varrentrapp Modified.**—This depends for its success on the fact that when nitrogenous substances are strongly heated with **sodium hydrate** they are decomposed, forming a carbonate and oxide with the oxygen from the hydroxyl, and liberating hydrogen, which then combines with the nitrogen to form **ammonia**. So as to prevent fusion of the glass tubes employed, solution of sodium hydrate is evaporated to dryness with calcium oxide, and the resulting mixture, known as **soda-lime**, is heated to redness and preserved for use.

(1) *Preliminary steps*:—

(*a*) Choose a combustion tube, about fifteen inches long and a half-inch bore, drawn and sealed as in fig. 38, and fitted with a perforated cork to take the bulbs.

(*b*) Measure out enough soda-lime to fill the tube and put it over the gas to get dry in a small basin and then cool under the desiccator. (If the soda-lime is already fresh and dry this is unnecessary, and we then only measure it out and put the quantity we want into a little dry stoppered bottle; but the quantity must always be measured, otherwise mistakes occur in filling the tube.)

(*c*) Put a glass mortar and a funnel with its limb cut off close to the neck on the top of the oven to warm.

(*d*) Put a little asbestos on to ignite, and then cool under the desiccator.

(*e*) Measure 20 c.c. of equivalent seminormal volumetric acid from a burette into a beaker. Take the "nitrogen bulbs" (fig. 41), and by sucking at the wide end with the narrow point immersed in the acid, transfer as much of it as possible to the bulbs without loss, and then cover the beaker up and set it aside.

(*f*) Weigh out ·4 to 2 grammes of the substance according to its richness in nitrogen.

(2) *Charging the tube.* This should be done over a sheet of glazed paper, so that anything spilt can be easily picked up without loss, and the short-ended funnel should be used to assist in filling the tube. About an inch of our soda-lime is first put in, then half of it is pounded up in the mortar with the weighed substance and transferred to the tube. The mortar is then rinsed with some more soda-lime, and these rinsings having been poured into the tube it is filled up with soda-lime to within two and a half inches of the end. A plug of asbestos is then put in, so as to leave about one inch free space between it and the charge, and the tube is laid on the table and tapped to cause a channel for gases at the top, as already described above.

(3) *Combustion.* The tube is placed in the furnace, and the bulbs having been attached by the perforated cork the first four burners are lighted. When the front is red-hot, the heat is gradually passed back as already described, carefully regulating the evolution of gases. When all the tube is red-hot and gases cease to pass, a piece of black rubber tube is slipped over the exit of the bulbs, and, suction being applied to it, the drawn-out end at the back of the combustion tube is broken

with a pair of tongs. A current of air is thus caused to pass through and to sweep all residual gases into the bulbs. The gas is then put out, and when cool the bulbs are detached and we then proceed to—

(4) *The titration.* The contents of the bulbs having been rinsed back into the same beaker as originally contained the acid (set aside for this purpose), taking care to wash the bulbs well and add the washings to the beaker, litmus is added, and the whole is titrated with seminormal soda, made to exactly balance the acid, and, the number of c.c. used having been deducted from 20, the difference is the c.c. of acid neutralised by the ammonia given off during combustion. Now 1 litre of equivalent normal acid (B.P. strength) would neutralise 16·94 grammes of NH_3 = 13·94 grammes of N; *e.g.* each c.c. would = ·01394 N for normal acid, ·00697 for seminormal acid, or ·003485 for quadrinormal; therefore, multiply the number of c.c. of acid neutralised by one of these factors according to the strength of acid employed, and the answer gives weight of N in the weight of substance taken, which is then calculated to percentage.

II. Original Method of Varrentrapp.—This was conducted in the same way, only the bulbs were charged with dilute HCl, and at the end of the combustion their contents were precipitated with $PtCl_4$ and the resulting precipitate of $PtCl_4(NH_4Cl)_2$ collected on a tared filter, dried at 100° C., weighed and calculated to N_2.

III. The Process of Dumas.—This consists in measuring the amount of pure nitrogen evolved, and is suitable for certain organic bases and for compounds containing nitrosyl (NO) or nitryl (NO_2), in which the soda-lime fails to convert all the nitrogen into ammonia.

The combustion tube (which in this case is twenty-six to twenty-eight inches long) is packed (1) with six inches of dry sodium hydrogen carbonate; (2) with a little pure cupric oxide; (3) with the weighed substance mixed with CuO; (4) with more pure CuO; and lastly with a considerable length of pure spongy metallic copper; and the whole is closed by a good cork, through which passes a bent delivery tube, dipping under the surface of mercury in a small pneumatic trough. Heat is first applied to the very end portion of the $NaHCO_3$, until sufficient CO_2 has been given off to entirely drive all the air out of the apparatus, which is ascertained by collecting a little of the gas passing off and seeing that it is entirely absorbed by solution of potassium hydrate. A graduated gas-collecting tube (fig. 42) is then filled, one-third with strong solution of KHO, and the remainder with mercury, and carefully inverted into the mercury trough so that no air is admitted, and placed over the mouth of the delivery tube. Combustion is now commenced at the front of the tube and gradually carried backwards as usual. The gases evolved are CO_2 and N, the former of which is absorbed by the KHO and the latter collects in the graduated tube. When the heat reaches the back, the remainder of the $NaHCO_3$ is decomposed, and the carbonic anhydride given off chases any trace of nitrogen out of the tube. The collecting tube is then closed by a small cup containing mercury, and transferred to the measuring trough (fig. 43), and entirely immersed therein. After leaving it until its contents have acquired the temperature of the water, it is raised so that the level of the water inside and outside the tube is equal, and the volume is read off. The temperature and pressure being noted, the weight of the nitrogen is obtained by the species of calculation already described at page 133.

IV. **Kjeldahl's Process.**—This method is rapidly superseding combustion. It depends upon the fact that when most nitrogenous bodies are heated with excess of strong sulphuric acid their nitrogen is converted into ammonium sulphate, from which latter the ammonia may be liberated by excess of alkali, distilled off and titrated. No special apparatus is really required other than a hard glass flask and the usual distilling arrangements; but where rapidity, combined with accuracy, is desired, the following special arrangements should be provided.

(1) Hard glass long-necked flasks, purchaseable as "Kjeldahl's flasks."
(2) A stand to hold the flasks in an inclined position over Bunsen burners.
(3) A distilling arrangement constructed as follows: A copper flask, capable of holding 500 c.c., is fitted with a rubber cork, through which passes the bottom end of a "Soxhlet" tube. The other end of this tube is closed by a rubber cork, pierced by two holes; through one of these passes the stem of a tapped funnel, and through the other the end of a block-tin tube, ⅜ inch in diameter, which is carried up to an altitude of 18 inches, and then brought down again, its other end passing through a rubber cork into a tapered glass connector, dipping to the bottom of a receiving flask, which latter is placed in a vessel of cold water. In this apparatus the "Soxhlet" acts as an anti-spurting appliance, and the use of a metal flask enables very rapid distillation to be performed. The receiving flask should be marked at 300 c.c., and should have a total capacity of about 400 c.c.

From 0·2 to 2·0 grms. of substance is taken (according to its richness in nitrogen), and is placed in a Kjeldahl flask, with 20 c.c. of strong sulphuric acid (free from nitrous compounds), and ·75 gramme of red mercuric oxide. The flask is placed on the stand and heated up to nearly the boiling-point of the acid for ten minutes. If the liquid should tend to become clear, no further addition is needed; but if it be still black, 5 to 10 grammes of potassium sulphate are added and the heating continued. When the liquid has become clear and colourless, or nearly so, the flask is allowed to cool, 200 c.c. water is added, and the whole poured into the funnel of the distilling apparatus. A further quantity of about 200 c.c. of water is used to rinse out the flask, and is also poured into the funnel, followed by 75 c.c. of 50 per cent. sodium hydrate solution and 20 c.c. of a 4 per cent. solution of potassium sulphide. The soda is to neutralise the sulphuric acid, and the potassium sulphide to prevent the formation of mercur-ammonium compounds. The stop-cock of the funnel is closed, and 50 c.c. of decinormal sulphuric acid having been placed in the receiving flask, the distillation is proceeded with. When the liquid in the receiver has risen to the mark the distillation is stopped, and its contents are titrated with decinormal alkali, using methyl-orange indicator. The number of c.c. of alkali used is deducted from 50, and the balance multiplied by ·001394 = nitrogen in the weight of substance started with. This nitrogen × 6·33 = the proteids present.

IV. ESTIMATION OF CHLORINE.

Chlorine is estimated by combustion of the substance in a tube filled with pure calcium oxide, when the chlorine displaces oxygen and turns part of the oxide into calcium chloride. After combustion the contents of the tube are dissolved in diluted nitric acid, filtered, and the Cl precipitated by argentic nitrate. (See Gravimetric Estimation of Chlorine, p. 151.)

V. ESTIMATION OF SULPHUR AND PHOSPHORUS.

Sulphur and phosphorus are estimated by fusing about 2 grammes of the solid substance in a silver crucible, with 24 grammes of pure potassium hydrate and 3 grammes of pure potassium nitrate. After fusion the sulphur and phosphorus (which have been converted into sulphates and phosphates respectively) are estimated by dissolving the residue in water, slightly acidulating with hydrochloric acid, and precipitating as usual. (See Gravimetric Estimation of Sulphates and Phosphates, p. 152.)

CHAPTER X.

THE ANALYSIS OF WATER, AIR, AND FOOD.

DIVISION I. THE SANITARY ANALYSIS OF WATER.

In the present state of our knowledge it is an open question whether a chemical analysis alone will under any circumstances enable a definite opinion to be formed as to the safety of any water supply unless supplemented by a bacteriological investigation. The latter, however, being evidently out of the province of this work, the chemical points are now given *quantum valeant.*

1. Collection of the Sample.

This is to be taken in a clean, stoppered "Winchester quart" bottle, previously entirely filled with the water, and emptied before finally filling up and introducing the stopper. The sample should be kept in a dark place, and analysed with as little delay as possible.

2. Colour.

This is to be judged by looking at a column of water in a colourless glass tube 2 feet long, and held over white paper. The presence of a greenish-yellow colour is an adverse indication.

3. Odour.

An 8-ounce wide-mouthed stoppered bottle, free from odour, is half filled with the water, warmed in the water bath to 38° C., shaken, and then the stopper is removed and the odour instantly noted. Peaty waters, and those containing marked amounts of sewage, can frequently be thus detected by a practised nose.

4. Suspended Solids.

Pass a litre of the turbid water through a dried and tared filter. Dry the filter and deposit at 120° C. and weigh. The gain in weight of the filter is the weight of suspended matter in a litre of water.

5. Total Solid Residue.

Heat a platinum basin of about 130 c.c. capacity to redness, cool it under the desiccator, and weigh. Introduce 100 c.c. of the water, and evaporate over a low gas flame until reduced to about 10 c.c.; then place it on the water bath till dry. Finally, heat it in the air bath at 105° C. until it ceases to lose weight, cool under the desiccator, and weigh. Having deducted the tare of the basin, the difference in milligrammes × 10 = total residue in parts per million, or the same × 7 ÷ 10 = grains per gallon. Example:—

Weight dish + residue	89·336
Tare of dish	89·300
	·036 or 36 milligrammes;

then $\frac{36 \times 7}{10} = 25{\cdot}2$ grains per gallon.

The residue should now be gradually heated to redness, and the presence of organic matter carefully looked for as indicated by charring; also the nature of the same, by whether the odour on burning is purely carbonaceous (like burning sugar) or nitrogenous (like burning hair). This latter is an especially unfavourable indication.

6. Chlorine.

Solutions required:

(*a*) 4·789 grammes *pure* crystallised argentic nitrate, dissolved in 1000 c.c. of distilled water. Each c.c. of this solution = ·001 (*one milligramme*) of chlorine.

(*b*) 5 grammes potassium chromate dissolved in 100 c.c. distilled water, and a weak solution of argentic nitrate dropped in until a slight permanent red precipitate is produced, which is allowed to settle in the bottle.

Process.—Put 100 c.c. of the water into a white basin, add a few drops of the chromate solution, and titrate with the silver solution from a burette, graduated in $\frac{1}{10}$ of c.c., until a faint permanent change of colour is produced, as already described (Chap. VII., p. 115). Note the number of c.c. used, multiply by 10, and the result will be chlorine in parts per million, or multiply by 7 and divide by 10, which will give grains per gallon. The water itself must be perfectly neutral; if acid it must be first shaken with a little pure precipitated chalk. The presence of a large amount of chlorine with excessive ammonia and albuminoid ammonia indicates that the organic impurity is, probably, of animal origin.

7. Nitrogen as Nitrates.

(*a*) *Crum Process.*—250 c.c. of the water are evaporated to a small bulk, the chlorine precipitated with saturated solution of argentic sulphate, filtered, and the filtrate concentrated in a basin to 2 c.c. A nitrometer (see p. 133) is charged with mercury, and the three-way stopcock closed, both to measuring tube and waste-pipe. The concentrated filtrate is poured into the cup at the top of the measuring tube, and the vessel which contained it rinsed with 1 c.c. of water, and the contents added. The stopcock is opened to the measuring tube, and, by lowering the pressure tube, the liquid is sucked out of the cup into the tube. The basin is again rinsed with 5 c.c. of pure strong sulphuric acid, and this is also transferred to the cup and sucked into the measuring tube. The stopcock is once more closed, and 12 c.c. more sulphuric acid put into the cup, and the stopcock opened to the measuring tube until 10 c.c. of acid have passed in. The excess of acid is discharged, and the cup and waste-pipe rinsed with water. Any gas which has collected in the measuring tube is expelled by opening the stopcock and raising the pressure tube, taking care no liquid escapes. The stopcock is closed, the measuring tube taken from its clamp and shaken by bringing it slowly to a nearly horizontal position and then suddenly raising it to a vertical one. This shaking is continued until no more gas is given off, the operation being complete in fifteen minutes. Now prepare a mixture of one part of water with five parts of sulphuric acid, and let it stand to cool. After an hour, pour enough of this mixture into the pressure tube to equal the length of the column of acidulated water in the working tube, bring the two tubes side by side, raise or lower the pressure tube until the mercury is at the same level in both tubes, and read off the volume of the nitric oxide. This volume, expressed in c.cs. and corrected to normal temperature and pressure, gives, when multiplied by ·175, the nitrogen in nitrates, in *grains per gallon*, if 250 c.c. of the water have been used. According to some authorities the precipitation of the chlorides is not necessary.

(*b*) *Copper-Zinc Process.*—This must be carried out as follows:—A wet copper-zinc couple is prepared by taking a piece of clean zinc foil, about 3 in. by 2 in., and immersing it in a solution of copper sulphate, containing about 3 per cent. of the pure crystallised salt. A copious and firmly adherent coating of black copper is speedily deposited upon the surface of the zinc, which must be allowed to remain in the solution until the deposit is thick enough, but not for too long a time, or it will become pulverulent and not adhere firmly to the zinc—three or four minutes will generally be sufficient.

The zinc coated with copper must then be removed from the solution and the couple thoroughly washed, first with distilled water, and finally with the water to be analysed, in order that this may replace the adhering distilled water. It is then put into a clean 6- or 8-ounce wide-mouthed stoppered glass bottle, and covered with 100 c.c. of the water to be analysed. If the water be very soft a small addition, say one part per 1000, of sodium chloride will accelerate the reaction. The stopper must then be inserted in the bottle and the water allowed to remain overnight in a warm place. If still greater speed be necessary the temperature may be raised to 90° or 100° F. (32° or 38° C.). With hard water it is preferable to add a small quantity of pure oxalic acid, to precipitate the lime and quicken the reaction. When the reduction is complete the fluid contents of the bottle are to be transferred to a retort with 200 c.c. of ammonia-free distilled water, and, the retort having been attached to a condenser, the contents are distilled till the distillate which comes over gives no colour with "Nessler." The distillate is then "Nesslerised," as already described (Chap. VII., page 136), and the number of milligrammes of NH_3 found are calculated to N (× 14 ÷ 17), and then the resulting milligrammes of N × 7 ÷ 10 = grains per gallon, or × 10 only = parts per million.

8. Nitrites.

Solutions required:—

1. Dilute sulphuric acid (1 of acid to 2 of water).
2. 5 grammes of metaphenylenediamine, and sufficient sulphuric acid to form an acid reaction dissolved in 1000 c.c. of water.
3. 0·406 grammes of pure dry silver nitrite dissolved in hot water, adding pure sodium chloride so long as a precipitate is formed, diluting to 1000 c.c. with water, and setting aside to deposit its silver chloride. 100 c.c. of the clear liquid are then diluted to 1 litre. 1 c.c. of this solution contains ·01 milligramme N_2O_3.

Process.—Put 100 c.c. of the water in a glass cylinder, and add 1 c.c. each of solutions 1 and 2. Prepare three other cylinders by diluting 5 c.c., 1 c.c., and 2 c.c. respectively, to 100 c.c. with pure water, and adding 1 c.c. each of solutions 1 and 2. Compare the shade of the water cylinder with that of the others, as described under "Nesslerising." The amount of N_2O_3 in the water is equal to that of the comparison cylinder having the same shade.

9. Ammonia and Albuminoid Ammonia.

These two indications are successively taken on the same quantity of water. The former is an estimation of the ammonia present in the water in the form of ammonium salts or similar compounds readily decomposed by a weak alkali, while the latter shows the ammonia derived from the decomposition of nitrogenous organic matter under the joint influence of an oxidising agent ($K_2Mn_2O_8$) and a hydrating agent (KHO), and is therefore a measure of the nitrogenous, and consequently presumably dangerous, organic matters contained in the water under examination.

The solutions and apparatus required are :—

(*a*) *Sodium carbonate.*
A 20-per-cent. solution of recently ignited pure sodium carbonate.

(*b*) *Alkaline potassium permanganate solution.*
Dissolve 200 parts of potassium hydrate and 8 parts of pure potassium permanganate in 1200 parts of distilled water, and boil the solution rapidly till concentrated to 1000 parts, cool, and keep in a well-stoppered bottle.

(*c*) *Distilled water which is free from ammonia.*
Distilled water which gives no reaction with Nessler test is pure enough. But, if this is not available, take the purest distilled water procurable, add pure ignited sodium carbonate in the proportion of 1 part per 1000, and boil briskly until at least one-fourth has been evaporated.

(*d*) A 40 ounce stoppered retort, with a neck small enough to pass loosely into the internal tube of a Liebig's condenser to the extent of 6 inches (see illustration, Chap. I., page 4). The joint between the retort and condenser is made by an ordinary india-rubber ring such as those used for the tops of umbrellas—which has been previously soaked in a dilute solution of soda or potash, being stretched over the retort tube in such a position that when the retort tube is inserted in the condenser it shall fit fairly tightly within the mouth of the tube about half an inch from the end.

(*e*) All the materials for "Nesslerising" (see Chap. VII., page 136).

The process is as follows :—

(*a*) *For ammonia.*—First test a little of the water with tincture of cochineal, to see if it shows an alkaline reaction. Put 500 c.c. of distilled water into the retort, and distil until 50 c.c. of the distillate gives no colour with 1½ c.c. of Nessler, thus rendering the whole apparatus "ammonia-free." Let the whole cool, pour out the distilled water (which may be saved for ammonia-free water), put in 500 c.c. of the water to be analysed, and, if it has not an alkaline reaction, make it alkaline with a drop or two of the sodium carbonate solution. The distillation should then be commenced, and not less than 100 c.c. distilled over. The receiver should fit closely, but not air-tight, into the condenser. The distillation should be conducted as rapidly as is compatible with a certainty that no spurting takes place. After 100 c.c. have been distilled over, the receiver should be changed, that containing the distillate being stoppered to preserve it from access of ammoniacal fumes. 100 c.c. measuring-flasks make convenient receivers. The distillation must be continued until 50 c.c. more are distilled over; and this second portion of the distillate must be tested with Nessler's re-agent to ascertain if it contains any ammonia. If it does not, the distillation for free ammonia may be discontinued, and this last distillate rejected; but, if it does contain any, the distillation must be continued still longer, until a portion of 50 c.c., when collected, shows no coloration with the Nessler test. The whole of the distillates must be mixed together and "Nesslerised" in the usual manner, and the total number of milligrammes of ammonia found are multiplied by 2, which gives milligrammes per litre (parts per million). This number in turn multiplied by 7 and divided by 100 gives grains per gallon of *ammonia*.

(*b*) *For albuminoid ammonia.*—As soon as the distillation above referred to has been started, 50 c.c. of the alkaline potassium permanganate solution are placed in a basin with 150 c.c. of distilled water, and boiled gently during the whole time that the free ammonia is distilling, adding some ammonia-free water if necessary, to prevent too much concentration. [The object of this is to ensure the entire evolution of any trace of ammonia present in the alkaline permanganate, thus avoiding a check analysis, as usually recommended.] At the same time a few fragments of clay tobacco-pipe are put into a platinum dish, heated to redness, and then kept warm till required for use. When the distillation of the ammonia is complete, take out the stopper of the retort and pour in the boiled alkaline permanganate by means of a perfectly clean funnel with a long limb; then remove the funnel and drop in the fragments of clay pipe. Now replace the stopper and continue the distillation, when the albuminoid ammonia will begin to come over. After 200 c.c. have been distilled, change the receiver and take off 50 c.c. at a time, as already described, until the last 50 comes over ammonia-free. Mix the distillates, "Nesslerise" and calculate as for the ammonia, noting the total result as albuminoid ammonia in parts per million or grains per gallon. Great care must be taken that no ammonia is kept in the room devoted to water analysis, and that all receivers used are first insured to be perfectly ammonia-free by proper rinsing with ammonia-free water and testing with Nessler.

10. Oxygen required to oxidise the Organic Matter.

Solutions required:—

(*a*) *Standard solution of potassium permanganate.*
Dissolve ·395 parts of pure potassium permanganate in 1000 of water. Each c.c. contains ·0001 gramme available oxygen.

(*b*) *Potassium iodide solution.*
One part of the pure salt recrystallised from alcohol, dissolved in 10 parts distilled water.

(*c*) *Dilute sulphuric acid.*
One part by volume of pure sulphuric acid is mixed with three parts by volume of distilled water, and solution of potassium permanganate dropped in until the whole retains a *very faint* pink tint, after warming to 27° C. for four hours.

(*d*) *Sodium hyposulphite.*
One part of crystallised sodium hyposulphite dissolved in 1000 parts of water.

(*e*) *Starch water.*
One part of starch to be intimately mixed with 500 parts of cold water, and the whole briskly boiled for five minutes, and filtered, or allowed to settle.

The Process.—Two separate determinations have to be made: *viz.*, the amount of oxygen absorbed during 15 minutes, and that absorbed during four hours; both are to be made at a temperature of 27° C. It is most convenient to make these determinations in 12-oz. stoppered bottles, which have been rinsed with sulphuric acid and then with water. Put 250 c.c. of the water into each bottle, which must be stoppered and immersed in a water-bath until the temperature rises to 27° C. Now add to each bottle 10 c.c. of the dilute sulphuric acid, and then 10 c.c. of the standard potassium permanganate solution. Fifteen minutes after the addition of the potassium permanganate, one of the bottles must be taken from the bath, and two or three drops of the solution of potassium iodide added to remove the pink colour. After thorough admixture add from a burette the standard solution of sodium hyposulphite, until the yellow colour is nearly destroyed, then introduce a few drops of starch water, and continue the addition of the hyposulphite until the blue colour is just discharged. If the titration has been properly conducted, the addition of one drop of potassium permanganate solution will restore the blue colour. At the end of four hours remove the other bottle, add potassium iodide, and titrate with sodium hyposulphite, as just described. Should the pink colour of the water in the bottle diminish rapidly during the four hours, further measured quantities of the standard solution of potassium permanganate must be added from time to time, so as to keep it markedly pink. The hyposulphite solution must be standardised, not only at first, but (since it is liable to change) from time to time in the following way:—To 250 c.c. of pure redistilled water, acidulated with 10 c.c. acid as before, add two or three drops of the solution of potassium iodide, and then 10 c.c. of the standard solution of potassium permanganate. Titrate with the hyposulphite solution, as above described. The quantity used will be the amount of hyposulphite solution, corresponding to 10 c.c. of the standard potassium permanganate solution, and therefore representing 1 milligramme of oxygen consumed. The difference between the number of c.c. of hyposulphite used in the blank experiment and that used in the titration of the samples of water multiplied by the amount of available oxygen contained in the permanganate added (= 1 milligramme if 10 c.c. have been used), and the product divided by the number of c.c. of hyposulphite corresponding to the latter as found by the check experiment, is equal to the amount of oxygen absorbed by the water.

Finally, the amount in milligrammes of oxygen absorbed, thus found, is multiplied by 4 for parts per million, and that result × 7 and ÷ 100 = grains per gallon.

11. Clark's Process for Hardness. Total *before boiling* and permanent *after boiling*.

Solutions, etc., required:—

(*a*) *Standard solution of calcium chloride.*

Made by dissolving 1 gramme of pure calcium carbonate in the smallest excess of hydrochloric acid, then carefully neutralising with dilute ammonia, and making the solution up to a litre with distilled water.

(*b*) *Standard soap solution.*

Dissolve 10 grammes of air-dried white Castile soap, cut into thin shavings, in a litre of dilute alcohol (sp. gr. 0·949).

To determine whether this solution contains the proper amount of soap, 10 c.c. of the solution of $CaCl_2$ are diluted with 60 c.c. of water, and the soap solution added till a persistent lather forms on agitation. If 11 c.c. of the soap solution have been used, it has the proper strength. If a greater or less quantity, it must be concentrated or diluted to proper strength. The soap solution, if turbid, must be shaken before using, but not filtered.

The Process.—(*a*) *For total hardness.* Put 70 c.c. of the water into the bottle, of 250 c.c. capacity, and add the soap solution gradually from a burette. After each addition of soap solution, the bottle is shaken and allowed to lie upon its side five minutes. This is continued until, at the end of five minutes, a lather remains upon the surface of the liquid in the bottle. At this time the hardness is indicated by the number of c.c. of soap solution added, minus one. If magnesium salts are present in the water the character of the lather will be very much modified, and a kind of scum (simulating a lather) will be seen in the water before the reaction is completed. The character of this scum must be carefully watched, and the soap test added more carefully, with an increased amount of shaking between each addition. With this precaution it will be comparatively easy to distinguish the point when the false lather due to the magnesium salt ceases, and the true persistent lather is produced. If the water is of more than 16° of hardness, mix 35 c.c. of the sample with an equal volume of recently boiled distilled water, which has been cooled in a closed vessel, and make the determination on this mixture of the sample and distilled water.

(*b*) *For permanent hardness.* To determine the hardness after boiling, boil a measured quantity of the water in a flask briskly for half an hour, adding distilled water from time to time to make up for loss by evaporation. It is not desirable to boil the water under a vertical condenser, as the dissolved carbonic acid is not so freely liberated. At the end of half an hour, allow the water to cool, the mouth of the flask being closed; make the water up to its original volume with recently boiled distilled water, and, if possible, decant the quantity necessary for testing. If this cannot be done quite clear, it must be filtered. Conduct the test in the same manner as described above.

The hardness is to be returned in each case to the nearest half-degree.

12. Judging the Results.

No definite rule can be laid down for judging all the results on one uniform scale, because the analyst ought to have special information as to the locality, nature of the soil, or depth of the well, before giving an opinion. For example, nitrates, which have in river and shallow surface waters the highest significance, as indicating the presence of previous sewage contamination, entirely lose such force in waters from deep artesian wells, because these are naturally rich in such salts. The same thing may be said of ammonia, which, although highly unfavourable in shallow waters, is yet always found in artesian wells, most probably from the metal pipes acting as reducing agents upon the nitrates. Again, with upland peaty waters we always find a large reduction of permanganate, and consequently an excess of "oxygen consumed," although the organic matter so acting cannot be viewed as dangerous.

Setting aside, however, all questions of mineral constituents and only looking at the indications of the presence or absence of organic matter, the author has devised a valuation scale, originally presented by him in a paper read before the Society of Public Analysts, and which has proved since that time as nearly correct as any general scale can be. The principle is to divide the amount of each figure found in the analysis by a fixed divisor, and *where the quotient exceeds* 10 *to double all figures over that number.* Let us suppose that, for example, a water yielded ·012 grain of albuminoid ammonia per gallon, and that the divisor fixed for this indication is ·0007; then we have—

$$\frac{\cdot 012}{\cdot 0007} = 17\cdot 1\text{; then } 17\cdot 1 - 10 = 7\cdot 1\text{, and } 7\cdot 1 \times 2 = 14\cdot 2\text{;}$$

therefore $14\cdot 2 + 10 = 24\cdot 2$, indicated degree of impurity.

To prevent the production of enormous figures, likely to startle non-professional persons, the indicated degree of impurity is expressed as a decimal by dividing it by 100. Thus, it is only when the article is very bad indeed that the indication comes into full numbers.

Taking, then, the whole scale, it stands as follows:—

GRAINS PER GALLON.

Ammonia	each ·0015 = 1.
Albuminoid Ammonia	,, ·0007 = 1.
Oxygen consumed in 15 minutes . . .	,, ·004 = 1.
Oxygen consumed in 4 hours . . .	,, ·010 = 1.

PARTS PER MILLION.

Ammonia	each ·02 = 1.
Albuminoid Ammonia	,, ·01 = 1.
Oxygen in 15 minutes	,, ·057 = 1.
Oxygen in 4 hours	,, ·143 = 1.

When any number exceeds 10, then all over 10 is to be doubled and added to the original number, and the total valuation is to be divided by 100 and noted as "comparative degree of organic impurity." Then, *supposing no* *other consideration intervenes to modify the analyst's opinion of the sample,* the following limits should be observed :—

1st Class Water	*up to* ·25 degree.
2nd ,, ,, (more or less questionable) .	*up to* ·50 ,,
Undrinkable Water	*over* ·40 ,,

DIVISION II. THE SANITARY ANALYSIS OF AIR.

For definite sanitary purposes it is really necessary to make a bacteriological as well as a chemical examination, but the former being outside the scope of this book, only the latter is considered. The chief points are :—

1. Testing for Gaseous Impurities.

The odour will call attention to these when present in notable proportions. Blotting paper dipped: (*a*) in tincture of turmeric, and introduced into the bottle containing the suspected air, turns red-brown in presence of ammonia; (*b*) in solution of subacetate of lead—black with sulphuretted hydrogen, or the vapour of ammonium sulphide; (*c*) in solution of sodium nitroprusside—purple with the vapour of ammonium sulphide, but no colour with H_2S; (*d*) in solution of potassium iodide mixed with starch paste—blue with chlorine or ozone or nitrous acid; (*e*) red litmus paper dipped in solution of potassium iodide—blue with ozone, but not with chlorine or nitrous fumes. A few drops of: (*a*) weak solution of indigo introduced into the bottle is decolourised by chlorine and sulphurous acid; (*b*) solution of barium chloride containing nitric acid is rendered turbid by sulphurous acid; (*c*) solution of argentic nitrate is rendered turbid by chlorine and not by nitrous fumes; (*d*) lime water is rendered slightly turbid by ordinary air, but becomes strongly milky with air containing an excess of carbonic acid. Air which is simply "foul" from sewage impurities or overcrowding will have a very characteristic "heavy" smell, and will decolourise a few drops of a *weak* solution of potassium permanganate, and will also show an excess of carbonic acid.

2. Estimation of Carbon Dioxide.

This is done by the method of Pettenkofer, which consists in standardising 100 c.c. of lime (or baryta) water with standard oxalic acid 2·25 grammes per litre, of which 1 c.c. = ·001 (1 milligramme of CaO). The air to be examined having been collected in a large bottle of known capacity, 100 c.c. of the same lime water are added, the bottle is closed, and well shaken for some time. The CO_2 is absorbed, forming $CaCO_3$. The resulting milky liquid is allowed to settle, and 50 c.c. are drawn off clear and immediately titrated with the same acid. The indicator is turmeric paper, or phenolphthalein, and the number of c.c. of acid used is multiplied by 2. The difference between the two titrations gives the amount of CaO precipitated as carbonate by the CO_2 in the air, and this is then calculated thus :—

$$\frac{\text{c.c. used} \times \cdot001 \times 44}{56} = CO_2 \text{ present in the volume of air taken.}$$

In strict analyses, the volume of air taken must be corrected for observed temperature and pressure to its volume at N.T.P. Normal air contains about ·04 per cent. of CO_2.

3. Estimation of Organic Matter.

A known volume of air is sucked by an aspirator through a specially arranged apparatus containing ammonia-free distilled water, and the resulting liquid is analysed for "free" and "albuminoid" ammonia like a water.

DIVISION III. FOOD ANALYSIS.

Here we will only attempt to consider a few of the more commonly occurring cases, always choosing the simplest and most rapid process.

1. Milk.

(1) **Specific Gravity.** Take the specific gravity at 60° F. If not at 60°, take the temperature and refer to the annexed table to get the true gravity at 60°, which will be found in the column opposite the observed gravity and under the observed temperature.

(2) **Total Solids.** Heat a small flat platinum dish about $1\frac{1}{2}$ inch in diameter to redness, cool it under the desiccator, and weigh. Put in 5 c.c. of the milk and again weigh. The difference = milk taken. Now transfer to the drying oven at 100° C. for 6 hours, cool under the desiccator and weigh. Put it back in the oven for an hour, repeat the cooling and weighing, and if the difference does not exceed a milligramme or two it is dry; if it does, then repeat the drying. The weight of the dish and dry residue *minus* the tare of the dish equals the total solids, which × 100 and ÷ by weight of milk taken = per cent. of total solids.

(3) **Fat.** Is got by using "Richmond's milk slide rule," an instrument constructed to automatically calculate by the following formula thus (T = total solids : G = specific gravity : F = fat) :—

$$T - \cdot254\ G = 1\cdot164\ F.$$

Deducting the fat thus found from the total solids, we get the "*solids not fat.*"

In event of the sample being the least sour, or when we are dealing with absolutely skimmed or "separated" milk, the rapid process above given fails. It is then necessary to extract the fat as follows :—10 grammes of the milk are weighed in a porcelain dish, 30 grammes of plaster of Paris are stirred in, and the whole is placed upon the top of the water bath and stirred occasionally till it appears dry. (When the sample is sour 2 drops of strong *liquor ammoniæ* are to be added to the milk in the dish before stirring in the plaster.) The mass is well powdered and introduced into a narrow-mouthed 8-ounce bottle with a well-fitting stopper, and 140 c.c. of pure ether having been rapidly poured in, the bottle is closed, shaken at intervals during two hours, and finally set aside in a cool place to settle during the night. In the morning, if the plastered milk was not over-dried, it will be found quite easy to pour off 70 c.c. of the ether perfectly clear into a weighed flask, from which the ether may then be distilled off, and the residual fat dried at 100° C. and weighed. The weight of fat found × 20 = percentage of fat in sample. Some analysts prefer to place the plastered milk in a paper cartridge and exhaust it with ether in the "Soxhlet's tube" (see Chap. I., p. 2), while others cause the milk to be soaked up into a roll of blotting paper, dried thereon, and then extracted in the "Soxhlet" with ether. This latter is the official process of the British Society of Public Analysts, but with ordinary milk nothing is so simple and good as the gravity, solids, and formula.

(4) **Added Water.** The limit for the strength of milk is at present based upon that of the poorest possible natural milk. Average milk will show :—

Fat . . .	3·00
Solids not fat . . .	9·00
Total	12·00

Observed Specific Gravity	DEGREES OF THERMOMETER (*Fahr.*).																				Observed Specific Gravity
	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	
1·020·0	19·2	19·3	19·4	19·4	19·5	19·6	19·7	19·8	19·9	19·9	1·020·0	20·1	20·2	20·2	20·3	20·4	20·5	20·6	20·7	20·9	21·0	1·020·0
1·021·0	20·2	20·3	20·3	20·4	20·5	20·6	20·7	20·8	20·9	20·9	1·021·0	21·1	21·2	21·3	21·4	21·5	21·6	21·7	21·8	22·0	22·1	1·021·0
1·022·0	21·2	21·3	21·3	21·4	21·5	21·6	21·7	21·8	21·9	21·9	1·022·0	22·1	22·2	22·3	22·4	22·5	22·6	22·7	22·8	23·0	23·1	1·022·0
1·023·0	22·2	22·3	22·3	22·4	22·5	22·6	22·7	22·8	22·8	22·9	1·023·0	23·1	23·2	23·3	23·4	23·5	23·6	23·7	23·8	24·0	24·1	1·023·0
1·024·0	23·2	23·3	23·3	23·4	23·5	23·6	23·6	23·7	23·8	23·9	1·024·0	24·1	24·2	24·3	24·4	24·5	24·6	24·7	24·9	25·0	25·1	1·024·0
1·025·0	24·1	24·2	24·3	24·4	24·5	24·6	24·6	24·7	24·8	24·9	1·025·0	25·1	25·2	25·3	25·4	25·5	25·6	25·7	25·9	26·0	26·1	1·025·0
1·026·0	25·1	25·2	25·2	25·3	25·4	25·5	25·6	25·7	25·8	25·9	1·026·0	26·1	26·2	26·3	26·5	26·6	26·7	26·8	27·0	27·1	27·2	1·026·0
1·027·0	26·1	26·2	26·2	26·3	26·4	26·5	26·6	26·7	26·8	26·9	1·027·0	27·1	27·3	27·4	27·5	27·6	27·7	27·8	28·0	28·1	28·2	1·027·0
1·028·0	27·0	27·1	27·2	27·3	27·4	27·5	27·6	27·7	27·8	27·9	1·028·0	28·1	28·3	28·4	28·5	28·6	28·7	28·8	29·0	29·1	29·2	1·028·0
1·029·0	28·0	28·1	28·2	28·3	28·4	28·5	28·6	28·7	28·8	28·9	1·029·0	29·1	29·3	29·4	29·5	29·6	29·8	29·9	30·1	30·2	30·3	1·029·0
1·030·0	29·0	29·1	29·1	29·2	29·3	29·4	29·6	29·7	29·8	29·9	1·030·0	30·1	30·3	30·4	30·5	30·7	30·8	30·9	31·1	31·2	31·3	1·030·0
1·031·0	29·9	30·0	30·1	30·2	30·3	30·4	30·5	30·6	30·8	30·9	1·031·0	31·2	31·3	31·4	31·5	31·7	31·8	32·0	32·2	32·2	32·4	1·031·0
1·032·0	30·9	31·0	31·1	31·2	31·3	31·4	31·5	31·6	31·7	31·9	1·032·0	32·2	32·3	32·5	32·6	32·7	32·9	33·0	33·2	33·3	33·4	1·032·0
1·033·0	31·8	31·9	32·0	32·1	32·3	32·4	32·5	32·6	32·7	32·9	1·033·0	33·2	33·3	33·5	33·6	33·8	33·9	34·0	34·2	34·3	34·5	1·033·0
1·034·0	32·7	32·9	33·0	33·1	33·2	33·3	33·5	33·6	33·7	33·9	1·034·0	34·2	34·3	34·5	34·6	34·8	34·9	35·0	35·2	35·3	35·5	1·034·0
1·035·0	33·6	33·8	33·9	34·0	34·2	34·3	34·5	34·6	34·7	34·9	1·035·0	35·2	35·3	35·5	35·6	35·8	35·9	36·1	36·2	36·4	36·5	1·035·0

If, however, a milk has only—

Fat	. . .	3·0
Solids not fat	. . .	8·5
	Total	11·5,

it will not be considered as definitely proved to be adulterated. In calculating the amount of water added the "solids not fat" are used for the basis of calculation because they are a fairly constant quantity, the fat being variable. The amount of pure standard milk present in any sample may be calculated thus:—

$$\frac{\text{Solids not fat} \times 100}{8·5} = \%\ \text{of pure milk present,}$$

and the difference between this result and 100 is, of course, added water.

(5) **Ash.** The total solids in the platinum dish are burned over a low flame at *dull* redness till quite white, and the ash is weighed. The ash should be about ·70 %, and it will never, as a rule, fall below ·67 in an unwatered milk.

(6) **Preservatives** are frequently added to milk, the favourite ones being *boric acid* and *formalin*, which can be detected as follows:—

(*a*) *Formalin* (formic aldehyd, 40 %) is detected by diluting the sample in a test tube with an equal volume of water, and then carefully running strong sulphuric acid down one side of the tube, so that about an inch layer of it forms at the bottom. On now *gently* agitating a violet shade will appear at the point of contact of the two liquids if formalin be present.

(*b*) *Boric acid* is detected in the ash of the milk by moistening with a drop or two of strong sulphuric acid, then adding alcohol and setting it on fire, when it will burn with a green flame in presence of boric preservative. To estimate the quantity we evaporate 100 grammes of milk to dryness, in a platinum dish, with 2 grammes of sodium hydroxide, and having thoroughly charred the residue we treat it with 20 c.c. of water and add HCl drop by drop till nothing more dissolves. We then wash from the dish into a 100 c.c. flask, taking care not to use more than 30 c.c. of water, and we then add ·5 gramme solid $CaCl_2$. To this we then add a few drops of phenol-phthalein, and drop in 10 per cent. solution of sodium hydroxide until a slight pink is produced, and then having added 25 c.c. of lime water, we make the whole up to the 100 c.c. mark and filter through a dry filter. To 50 c.c. of this filtrate (= 50 grammes milk) we add N sulphuric acid till the colour is discharged, then add methyl-orange indicator, and continue to add the acid till a faint pink is produced, and lastly we drop in $\frac{N}{2}$ alkali till the liquid assumes the yellow tinge. At this stage all acids other than boric likely to be present are in a state neutral to phenol-phthalein. The solution having been cooled, is mixed with some phenol-phthalein and 33 % of glycerine (to set free boric acid), and is titrated with $\frac{N}{2}$ alkali, each c.c. of which consumed = ·0124 crystallised boric acid in 50 grammes of milk, and this × 2 = per cent.

(7) **Sour Milks** that will not readily become homogeneous should have one drop of *liquor ammon. fort.* added to each ounce, before shaking, when a sufficiently fair sample will be generally obtainable for analysis. Sour milks are generally from ·2 to ·3 too low in the "solids not fat," and the results are not really properly comparable with those from fresh milk, so caution is necessary in forming opinions on sour samples, unless the departure from the standard is very marked.

2. Butter.

The only really serious adulteration of butter consists in mixing it with other fats of lower commercial value. Such a mixture may be legally sold if labelled "margarine."

The butter is to be first melted in a beaker on the top of the water bath, when it will gradually separate with a top layer of clear butter-fat, and a bottom one of water and curd. If the top layer of fat does not become quite clear it must be filtered through a dry filter placed over a beaker inside the water oven, but it will often clear sufficiently to enable enough to be poured off without filtering, and, speaking generally, the better the butter the more easily the fat will clarify.

Having thus got the actual fat ready for analysis we counterbalance a small flask of about 250 c.c. capacity, and having a mark at 150 c.c., and weigh into it 5 grammes of the clarified fat and then add 50 c.c. of a solution of potassium hydrate in alcohol (S.V.R.) having a strength of 30 grammes per litre (3 per cent.). The flask having been closed by a cork through which passes a piece of narrow glass tube, its contents are heated on the water bath, with constant agitation, until the fat is entirely dissolved. The flask is then attached to a condenser, and the alcohol entirely distilled off. The residual soap thus left in the flask is dissolved in a little hot water, and 25 c.c. of diluted sulphuric acid of 5 per cent. strength having been added, the whole is made up by distilled water to the 150 c.c. mark. A few fragments of recently ignited pipe-clay having been dropped in, the flask is connected to a short condenser and the contents distilled until the distillate measures 100 c.c. This distillate is then filtered, and a few drops of solution of phenol-phthalein having been added the whole is titrated with decinormal solution of sodium hydrate or with vigintinormal baryta water, which latter is preferred by some analysts; 5 grammes of pure butter-fat thus treated yields a distillate requiring not less than 25 c.c. of decinormal soda, while lard, tallow, and the other solid animal fats do not take more than 1·5 c.c. The only fat coming anywhere near butter is cocoa-nut fat, which takes about 7 c.c., because it also contains fatty acids, volatile at the heat of boiling water. To calculate the amount of butter present in any mixture we multiply the number of c.c. of soda used by 100 and divide by 25. Certain exceptional butters having been met with, during the winter months, which only consumed 21 c.c., no definite expression of opinion can safely be given unless the article takes less than that number of c.c. of decinormal soda.

3. Taking the Alcoholic Strength of Spirits, Tinctures, Wines, Beer, and all Alcoholic Liquids.

If the sample is simply one of pure diluted alcohol we ascertain its specific gravity, taking care that the temperature of the liquid is exactly 60° F. We then look at the annexed table and find the strength of the spirit. It, however, frequently happens that it is not possible to get the sample exactly to 60° F., and in such a case we must carefully note the temperature at which we worked and make a calculated correction for the expansion of the spirit, based on the following data:—

If the spirit be above 70 per cent. of apparent strength, then we must add ·0005 to the specific gravity for each degree F. that the spirit was above

(3) **Table for ascertaining the percentages respectively of Alcohol by Weight, by Volume, and as Proof Spirit, from the Specific Gravity.**

Specific gravity, at 60° F	Absolute Alcohol by weight Per cent	Absolute Alcohol by volume Per cent	Proof Spirit. Per cent
1·000	0·00	0·00	0·0
·999	0·55	0·65	0·1
·998	1·05	1·30	2·4
·997	1·60	2·00	3·5
·996	2·15	2·70	4·9
·995	2·75	3·50	6·1
·994	3·30	4·15	7·2
·993	3·90	4·90	8·6
·992	4·50	5·65	9·9
·991	5·15	6·40	11·2
·990	5·75	7·15	12·6
·989	6·40	8·00	14·1
·988	7·10	8·80	15·5
·987	7·80	9·65	16·9
·986	8·50	10·55	18·4
·985	9·20	11·40	20·0
·984	9·90	12·35	21·5
·983	10·65	13·20	23·1
·982	11·45	14·10	24·7
·981	12·25	15·10	26·5
·980	13·00	16·00	28·0
·979	13·80	17·00	29·8
·978	14·65	18·00	31·6
·977	15·45	19·00	33·3
·976	16·30	20·00	35·1
·975	17·10	21·00	36·8
·974	17·90	21·95	38·5
·973	18·80	23·05	40·5
·972	19·55	23·90	42·0
·971	20·35	24·90	43·6
·970	21·10	25·75	45·2
·969	21·95	26·85	46·9
·968	22·75	27·75	48·6
·967	23·50	28·65	50·2
·966	24·25	29·55	51·8
·965	25·00	30·40	53·3
·964	25·70	31·20	54·7
·963	26·45	32·05	56·2
·962	27·15	32·90	57·6
·961	27·80	33·65	59·0
·960	28·45	34·40	60·3
·959	29·10	35·10	61·6
·958	29·70	35·80	62·8
·957	30·35	36·55	64·1
·956	31·00	37·35	65·4
·955	31·55	37·95	66·5
·954	32·15	38·60	67·6
·953	32·70	39·20	68·7
·952	33·30	39·90	70·0
·951	33·80	40·55	71·0
·950	34·40	41·20	72·2
·949	35·00	41·85	73·3
·948	35·50	42·40	74·3
·947	36·05	43·00	75·4
·946	36·55	43·60	76·4
·945	37·10	44·15	77·4
·944	37·65	44·75	78·4
·943	38·20	45·40	79·5
·942	38·65	45·85	80·4
·941	39·15	46·40	81·4
·940	39·70	47·00	82·4
·939	40·15	47·50	83·3
·938	40·65	48·05	84·1
·937	41·15	48·60	85·1
·936	41·65	49·10	86·1
·935	42·15	49·65	87·0
·934	42·65	50·15	87·9
·933	43·15	50·70	88·9
·932	43·60	51·20	89·8
·931	44·10	51·70	90·6
·930	44·55	52·15	91·4
·929	45·00	52·70	92·3
·928	45·50	53·15	93·2
·927	45·95	53·65	94·1
·926	46·40	54·10	94·8
·925	46·90	54·60	95·6
·924	47·30	55·10	96·5
·923	47·80	55·55	97·4
·922	48·25	56·05	98·2
·921	48·65	56·50	99·0
·920	49·15	56·95	99·8
·9198	49·25	57·05	100 OPS
·919	49·65	57·40	100·6
·918	50·10	57·90	101·5
·917	50·55	58·40	102·3
·916	51·00	58·85	103·1
·915	51·45	59·30	103·9
·914	51·90	59·75	104·7
·913	52·35	60·15	105·5
·912	52·80	60·65	106·5
·911	53·25	51·05	107·0
·910	53·65	61·50	107·8
·909	54·10	61·95	108·5
·908	54·55	62·40	109·3
·907	54·95	62·80	110·0
·906	55·45	63·30	110·9
·905	55·90	63·70	111·6
·904	56·35	64·10	112·3
·903	56·75	64·55	113·1
·902	57·20	65·00	113·9
·901	57·60	65·35	114·6
·900	58·05	65·80	115·4
·899	58·55	66·30	116·2
·898	58·95	66·65	116·8
·897	59·35	67·05	117·5
·896	59·85	67·55	118·4
·895	60·30	68·00	119·2
·894	60·70	68·35	119·8
·893	61·10	68·75	120·5
·892	61·55	69·15	121·1
·891	62·00	69·55	121·9
·890	62·45	69·95	122·6
·889	62·85	70·35	123·3
·888	63·25	70·75	124·0
·887	63·70	71·20	124·7
·886	64·15	71·60	125·4
·885	64·55	71·90	126·0
·884	65·00	72·35	126·3
·883	65·40	72·75	127·5
·882	65·80	73·15	128·2
·881	66·25	73·50	128·9
·880	66·65	73·90	129·6
·879	67·05	74·30	130·2
·878	67·55	74·70	130·9
·877	67·95	75·10	131·6
·876	68·40	75·45	132·2
·875	68·80	75·80	132·9
·874	69·20	76·15	133·5
·873	69·65	76·60	134·3
·872	70·05	76·95	134·9
·871	70·50	77·35	135·6
·870	70·85	77·65	136·1
·869	71·30	78·10	136·6
·868	71·75	78·45	137·4
·867	72·20	78·75	138·1
·866	72·55	79·15	138·8
·865	73·00	79·55	139·4
·864	73·45	79·95	140·1
·863	73·80	80·25	140·7
·862	74·25	80·60	141·3
·861	74·70	81·00	141·9
·860	75·10	81·35	142·6
·859	75·50	81·70	143·2
·858	75·80	81·95	143·8
·857	76·30	82·40	144·4
·856	76·70	82·75	145·0
·855	77·15	83·15	145·6
·854	77·55	83·45	146·2
·853	78·00	83·80	146·7
·852	78·40	84·15	147·4
·851	78·80	84·45	148·0
·850	79·20	84·84	148·6
·849	79·60	85·15	149·1
·848	80·05	85·50	149·7
·847	80·45	85·90	150·3
·846	80·80	86·15	150·9
·845	81·20	86·50	151·5
·844	81·65	86·80	152·1
·843	82·00	87·10	152·7
·842	82·45	87·45	153·2
·841	82·80	87·75	153·8
·840	83·20	88·05	154·3
·839	83·60	88·35	154·9
·838	84·00	88·65	155·4
·837	84·40	89·00	156·0
·836	84·80	89·30	156·5
·835	85·20	89·60	157·1
·834	85·60	89·95	157·6
·833	85·95	90·25	158·1
·832	86·35	90·55	158·6
·831	86·75	90·85	159·1
·830	87·15	91·10	159·7
·829	87·50	91·40	160·2
·828	87·90	91·70	160·7
·827	88·30	92·00	161·2
·826	88·65	92·30	161·7
·825	89·05	92·55	162·2
·824	89·50	92·90	162·8
·823	89·90	93·25	163·4
·822	90·25	93·50	163·9
·821	90·65	93·75	164·3
·820	90·95	94·00	164·7
·819	91·35	94·25	165·1
·818	91·70	94·50	165·6
·817	92·05	94·75	166·1
·816	92·45	95·00	166·5
·815	92·80	95·25	167·0
·814	93·20	95·50	167·4
·813	93·55	95·80	167·9
·812	93·95	96·10	168·4
·811	94·30	96·35	168·8
·810	94·60	96·55	169·2
·809	94·95	96·80	169·6
·808	95·30	97·05	170·0
·807	95·70	97·25	170·4
·806	96·00	97·50	170·8
·805	96·35	97·70	171·2
·804	96·70	97·95	171·6
·803	97·03	98·15	172·0
·802	97·35	98·40	172·4
·801	97·70	98·55	172·7
·800	98·00	98·75	173·1
·799	98·35	99·00	173·5
·798	98·65	99·20	173·8
·797	98·95	99·40	174·1
·796	99·30	99·55	174·4
·795	99·60	99·75	174·8
·794	99·95	99·95	175·2
Absolute Alcohol.			
·7938	100·00	100·00	175·25

60° F., or we must deduct the same amount for each degree that the spirit was below 60°. This will now give the real gravity at 60° F., and a reference to the table will show the true strength. If the spirit is below 70 per cent., we must then use smaller amounts to add or deduct as follows :-

Under 70 but over 40 add or deduct ·0004 for each degree F.
" 40 " 25 " ·0003 " "
" 25 " 15 " ·0002 " "
" 15 " 0 " ·0001 " "

When we are operating on a wine, tincture, or other complex alcoholic liquor, the spirit it contains must be distilled off and the specific gravity of the distillate ascertained. To do this we take 50 c.c. of the sample, and having carefully taken its temperature and noted the same, we transfer it to a small retort attached to a condenser, rinsing out the measuring flask with two successive quantities of 5 c.c. each of distilled water. We then place the same measuring flask at the end of the condenser and distil until 40 c.c. have passed over. 10 c.c. of distilled water are now to be added to the contents of the retort, and the distillation is to be continued until very nearly 50 c.c. have been distilled over. The temperature of this distillate having been brought to the same degree as that at which the sample was measured, distilled water is to be added exactly up to the 50 c.c. mark. By this means it is possible to obtain a volume of pure spirit of precisely the same strength as the sample, and we finally take the specific gravity of the same and apply the tables as above directed. Some chemists prefer to distil off three-fourths of the sample, and having taken the specific gravity of the distillate, to add some water and distil off the remaining fourth, taking its gravity separately, and finally adding the results both together.

4. Bread and Flour.

Take 10 grammes of the bread in a weighed platinum dish, and dry it in the water oven for 3 hours at a temperature of 100 C. Good bread should not lose more than 44 per cent. of its weight. Now place the dish over the Bunsen burner and heat it to redness until it is reduced to a uniformly greyish-white ash and again weigh. This ash should not weigh more than 1·5 per cent. of the original bread.

Note. - Both bread and flour are very difficult to burn, and it is better to first char them to a mass of coke, then to remove this mass to a glass mortar and powder it, and finally to return the powder to the platinum dish to finish.

Acidity. Put 20 grammes of bread (or 10 grammes of flour) into an 8-oz. wide-mouthed stoppered bottle, and pour in 200 c.c. of rectified spirit ; close the bottle and let it stand some hours. Then pour off 100 c.c. of the clear liquor, add a drop of solution of phenol-phthalein and run in decinormal solution of soda until a pink tint is produced. Good fresh bread or flour should not require more than 1 c.c. of the soda solution to render it alkaline.

Alum. Mix together 5 c.c. of freshly prepared tincture of logwood with 5 c.c. of a saturated solution of official carbonate of ammonia and 50 c.c. of water, and at once pour it on to a mass of the bread taken from the inner portion of the loaf. If a fair adulteration of alum be present a slate-blue colour will be produced, but if the amount of alum be small (say less than 10 grains per 4-lb. loaf) then the colour will only appear after gently warming on the top of the water oven for some time. If the presence of alum be shown by this test, its amount must be estimated as follows : 100 grammes of the bread are burned to ash in a platinum dish, and when cold 5 c.c. of fuming hydrochloric acid are added, and the dish having at once been covered by a glass plate the whole is allowed to stand for 15 minutes ; 25 c.c. of water are then added to the dish and its contents are gently boiled for five minutes and filtered. The insoluble matter (chiefly silicious matter and clay) having been washed and the washings added to the filtrate, the latter is mixed with 5 c.c. of strong liquor ammoniæ and 40 c.c. of acetic acid. The ash of bread being rich in phosphoric acid, the precipitate thus produced will consist of aluminium phosphate with some ferric phosphate; and such precipitate must then be filtered off, washed, dried, ignited, and weighed. If this precipitate does not exceed 5 milligrammes it is not worth going farther, but if it does, we must then proceed to estimate the iron present in it by the colourimetric method given at page 126. The ferric chloride solution used should contain an amount of iron equivalent to one-tenth of a milligramme of ferric phosphate in each c.c. After the iron has been estimated and deducted from the original weight of the precipitate, each milligramme remaining may be taken as representing one grain of alum per 4-lb. loaf.

Alum and other mineral impurities added to flour are best detected by shaking up some of the sample with chloroform in a separatory funnel, and then letting it stand, when the flour will float on the top, and the sand, alum, and other mineral matters will sink to the bottom.

5. Mustard.

This is chiefly a microscopical matter for the exact identification of impurities, but the following chemical operations may be performed:—

(1) Test a cooled decoction for starch with solution of iodine.

(2) If starch be found, extract a weighed portion in the "Soxhlet" with petroleum spirit or ether. Distil off the spirit, dry and weigh the oil. Mustard contains as an ordinary minimum 33 % of oil, and the amount of genuine mustard in the sample will then be found thus:—

$$\frac{\%\text{ of oil found} \times 100}{33} = \%\text{ genuine mustard;}$$

by deducting this from 100 the difference is added starch or flour.

(3) Moisten the mustard with a little ammonia, when the turmeric brown will be developed if that colouring agent be present.

6. Pepper.

Mineral Impurities. Weigh out 10 grammes of the sample in a tared platinum dish and ignite it to a perfect ash, as already described under bread, and weigh. If the ash does not much exceed 2 per cent. in white, or 5 per cent. in black pepper, it may be passed, but if it does, the contents of the dish must be boiled with diluted hydrochloric acid, and the insoluble matter having been collected on a filter, and washed until free from acidity, is to be dried, ignited, and weighed. Any insoluble matter thus found over 4·5 per cent. may be considered to represent adulteration with sand.

Vegetable Impurities. These are rendered visible under the microscope by mounting some of the sample with a drop of an acid solution of aniline acetate, which stains poivrette (ground olive stones) and other woody impurities yellow, without affecting the detection of any rice flour or other cereal that may be present. If they be found we can get a fair idea of their amount by estimating the amount of matter soluble in alcohol (resin, piperine, etc.), present in the sample as follows:—2 grammes of the pepper are boiled in a long-necked flask with 40 c.c. of absolute alcohol for ten minutes and the solution passed through a filter placed over a large platinum dish, the insoluble matter on the filter being washed with another 25 c.c. of alcohol. The dish is placed on the water bath until the spirit has passed off, and the residue is dried for half an hour at 100° C. and weighed. Lastly, it is placed over the "Bunsen" and ignited, cooled, and again weighed and the weight deducted from the former one. The difference is the weight of the extract, which should not be less than 8 per cent. in white, or 10 per cent. in black pepper. If, for example, the extract of a sample of white pepper, in which rice starch had been found by the microscope, only amounted to 4 per cent., we should then charge it with being adulterated to the extent of 50 per cent.

In the case of poivrette or excessive bleached pepper husk being found in a sample, we boil one gramme for an hour with 100 c.c. of water, and 2 c.c. of sulphuric acid under an upright condenser for an hour, cool and filter through a pair of counterbalanced filters, wash till every trace of acidity has been removed, and dry the filters and their contents to constant weight in the water oven. Pure pepper thus treated yields not more than 35 per cent. of insoluble matter, while husks and poivrette yield 70 and 75 per cent. respectively. The calculation is manifest—thus, suppose a sample (in which much husk was seen under the microscope) to show 52·5 per cent. of insoluble matter, it would contain 50 per cent. of added husks. A not uncommon recent adulteration of pepper consists in adding ground ginger which has been already exhausted by spirit to make the essence of ginger.

7. Coffee.

If chicory be found by a microscopic examination of the sample—best done after boiling with dilute NaHO—10 grammes of the coffee are placed in a flask with 100 c.c. of distilled water. The flask is counterbalanced, and then boiled for a quarter of an hour. It is then placed on the scales, and the original balance is restored by adding water. Finally the decoction is filtered, cooled to 15·5° C., and its specific gravity is taken. The gravity of pure coffee does not exceed 1009·5, while that of chicory solution is 1021·7. Supposing, therefore, that a decoction showed a gravity of 1015·5, then—

$$1021{\cdot}7 - 1009{\cdot}5 = 12{\cdot}2, \text{ and } 1015{\cdot}5 - 1009{\cdot}5 = 6{\cdot}0$$

therefore—

$$12{\cdot}2 : 6 :: 100 = 49 \text{ per cent. of chicory.}$$

8. Coloured Sweets.

The poisonous colours are nearly all mineral and insoluble. They may be scraped off, washed with water, and identified by the ordinary methods given in Chapter IV. As a rule, at present, only aniline colours are used, and they are added in such minute proportions as not to be considered dangerous.

9. Direct Estimation of Starch in Cereals.

This depends upon the fact that starch forms an insoluble compound with barium. If an excess of baryta water of known strength be added to starch which has been gelatinised in water, a portion of the barium will combine with the starch, and then by estimating the excess of baryta water left unabsorbed we can find the amount taken up by the starch. The formula of the starch-baryta compound is $C_{24}H_{40}O_{20}$, BaO, and it therefore contains 19·1 per cent. of BaO.

The materials required are:—

(1) Decinormal hydrochloric acid, containing 3·65 grammes real HCl per 1000 c.c. = ·00765 BaO for each c.c.

(2) Baryta water kept in a special jar with a burette permanently attached, as shown in the illustration below. A is the jar for the baryta water, having a tube attached containing lumps of quicklime to prevent the entrance of CO_2 from the air. The burette (B) is attached to the bottom neck of the jar by a tube having a pinchcock (*a*) to admit the reagent, and a tube (*n*) filled with lumps of caustic potash to prevent entrance of CO_2.

(3) Alcoholic solution of phenol-phthalein as an indicator.

The Process.—The substance is powdered or finely ground in a mill, and 3 grammes weighed out for analysis. If (as in the case of mustard, pepper, etc.) it contains oil or resinous bodies, these are first extracted by percolation with petroleum spirit or ether in the "Soxhlet." The powder is then well rubbed up with successive quantities of water until thoroughly disintegrated, the liquid being transferred to a 250 c.c. flask, and 100 c.c. of water in all being used to entirely transfer the powder from the mortar to the flask. In dealing with very hard substances, like beans, peas, etc., the water should be used boiling. The flask and contents are now heated on the water bath for half an hour, with frequent shaking, to *entirely gelatinise* the starch. The whole is then cooled, and, 50 c.c. of standard baryta water having been added from the burette, the flask is corked, well shaken for two minutes, proof spirit is added up to the 250 c.c. mark, and the whole again shaken, *tightly corked*, and set aside to settle. While settling, a check is made on 50 c.c. of the baryta water by shaking up with 100 c.c. of freshly boiled distilled water, in a 250 c.c. corked flask, and then titrating with the decinormal HCl, in the presence of two drops of phenol-phthalein. The number of c.c. of acid used is recorded, giving the total strength of 50 c.c. of the baryta water employed. When the main analysis has settled, 50 c.c. of the clear liquid are drawn off with a pipette, rapidly titrated with the decinormal acid and phenol-phthalein, as in the check, and the number of c.c. of acid used is multiplied by 5 and set down as strength of baryta water remaining uncombined. This latter amount is deducted from the total check strength, and the difference in c.c. of acid is multiplied by ·00765, which gives BaO combined with the starch. This result now multiplied by 4·2353 gives the amount of starch in the 3 grammes taken = x: then

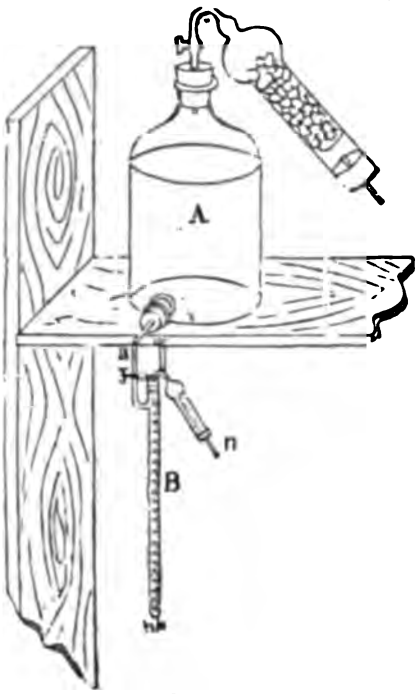


Fig. 45.

$$\frac{x \times 100}{3} = \text{percentage of starch.}$$

10. Free Sulphuric Acid in Vinegar.

To a dilute solution of methyl violet add a drop of vinegar. A blue colour shows the presence of a mineral acid in the sample.

Mix 50 c.c. of the vinegar with 25 c.c. of volumetric solution of sodium hydrate, made decinormal by diluting the normal volumetric solution to ten times its bulk with water. The whole is evaporated to dryness, and incinerated at the lowest possible temperature. 25 c.c. of decinormal solution of oxalic acid (made to exactly balance the sodium hydrate solution) are now added to the ash, the liquid heated to expel CO_2, and filtered. The filter is washed with hot water, and the washings having been added to the filtrate, phenol-phthalein solution is added, and the amount of free acid ascertained by running in decinormal soda from a burette. The number of c.c. of soda thus used multiplied by ·0049 gives the amount of free sulphuric acid in the vinegar. This process depends on the fact that *whenever the ash of vinegar has an alkaline reaction, free mineral acid was undoubtedly absent.*

CHAPTER XI.

ANALYSIS OF DRUGS, FIXED AND ESSENTIAL OILS, FATS, WAXES, SOAPS, DISINFECTANTS, URINE, AND URINARY CALCULI.

DIVISION I. ANALYSIS OF DRUGS.

I. GENERAL SCHEME.

THE analysis of drugs is so large a subject that only a few of the more commonly occurring problems can be discussed in the present volume. It will, however, be interesting, before proceeding to the consideration of special matters, to give a sketch of the general method of analysing a vegetable substance used in medicine, following the lines laid down by Dragendorff.

Step I. Dry a weighed portion of the substance in the water oven until it ceases to lose weight.

Step II. Pack the dried and powdered substance, mixed with a little sand, in a "Soxhlet" apparatus, thoroughly exhaust it with petroleum spirit, and cork up and save the fluid extract so obtained, marking it A.

Step III. Spread the solid left from Step II. out to dry on a plate of glass on the top of the water oven, and when all odour of petroleum has passed off, replace it in the Soxhlet, and exhaust it this time with perfectly anhydrous ether. Cork up the ethereal extract obtained and mark it B.

Step IV. Spread out as before, and when all odour of ether is gone re-pack and extract with purified commercial methyl alcohol, as sold for making methylated spirit. This is more volatile than common alcohol, and is as a rule a better solvent of the articles required in this group, while it does not so readily extract glucose, etc. It is an article of commerce, and can be specially ordered through a purveyor of chemicals as "commercial methol, highest strength." Save this alcoholic extract and mark it C.

Step V. Extract the insoluble matter from Step IV. with distilled water at a temperature not exceeding 120° Fahr., and filter. Wash with cold water and save the filtrate (D).

Step VI. Wash the insoluble matter off the filter into a large flask, with plenty of water, acidulated with 1 per cent. of hydrochloric acid, and boil it for an hour under an upright condenser. Let it settle, pour off the liquid as close as possible (saving it), and then collect the insoluble matter on a filter and wash with boiling water, adding the washings to what was poured off. This extract is marked E.

Step VII. Once more wash the insoluble matter from the filter into a beaker and boil it up for an hour with plenty of water rendered distinctly alkaline with sodium hydrate. Collect on a weighed filter, wash first with boiling water, acidulated with hydrochloric acid, and then with plain boiling water, till no trace of a chloride remains; dry in the water oven and weigh, deducting the tare of the filter. Lastly, ignite the filter and its contents in a weighed platinum basin, and deduct the ash so found from the first weight, and the difference will be a woody fibre in the drug.

Step VIII. Make a *nitrogen* determination by Kjeldahl's method (page 166) on a fresh portion, and the nitrogen found (after deducting any due to alkaloids present) multiplied by 6·33 will give the amount of albuminous bodies present.

Treatment of the Separate Solutions.—Each liquid is made to a definite number of c.c. with the same solvent, and then an aliquot part, say 10 c.c., is taken and evaporated, and the residue weighed, to find the total matter soluble in each solvent. The remainders of the liquids are then treated as follows:—

Liquid A. This will contain chiefly fixed and volatile oils. The spirit is allowed to evaporate spontaneously, or in a current of cold dry air, and the residue is distilled with water, when the volatile oil passes over, leaving the fixed oil in the retort.

Liquid B. This chiefly contains resins, together with some bitters, alkaloids, and organic acids. The solution is evaporated to dryness on the water bath with sand, and the residue, having been powdered, is boiled with water slightly acidulated with HCl. A portion of this watery solution is tested for benzoic, cinnamic, salicylic, gallic, and other free organic acids, and the remainder is saved for subsequent use in Group C. The portion insoluble in water now chiefly represents any resins present in the drug, which are soluble in ether. These may be further divided and examined by the action of alcohol. Resins are recognised by their behaviour with solvents, their odour on warming, and by the action of H_2SO_4, HNO_3, HCl, etc., on spots of the solid resin left by evaporating the solutions. This matter requires special experience; but a description of the nature and reactions of all the principal resins will be found in any large book on Materia Medica.

Liquid C. Is evaporated to a low bulk, and then poured into water faintly acidulated with hydrochloric acid. Any insoluble matter is probably a resinous body insoluble in ether, and is to be filtered out and examined as a resin. A portion of the aqueous solution is to be tested for tannin, and the remainder is to be mixed with the reserved liquid from B, the whole gently evaporated to a convenient bulk, and treated by immiscible solvents as follows:—

Step I. The liquid (which must still retain a slightly acid reaction) is shaken up successively with chloroform and ether in a separator (see fig. 17, page 93). The solvents are drawn off and evaporated, and the residues so obtained tested for glucosides and bitter principles.

Step II. The liquid remaining in the separator is now rendered alkaline with sodium hydrate and again shaken up with chloroform. This extracts nearly all the alkaloids. The chloroform is evaporated and the residue tested for alkaloids (see Chap. V.).

Step III. The liquid still remaining in the separator is shaken up with warm amylic alcohol, which takes out morphine and leaves it on evaporation, when any residue is tested for its presence.

Liquid D. Is evaporated to a low bulk and then mixed with twice its volume of rectified spirit, when gums precipitate insoluble and may be examined, and sugars dissolve and may be estimated by "Fehling." Saponin also may be found with the sugars.

II. ALKALOIDAL ASSAY BY IMMISCIBLE SOLVENTS.

The immiscible solvents usually employed in the assay of alkaloids are chloroform, ether, benzin (petroleum spirit), benzol (benzene), and amylic alcohol, or a mixture of the latter two called benzolated amylic alcohol. The liquids are not miscible with water, but can be diffused through it by shaking, and then separate from it when set at rest. It is a general property of alkaloids that they themselves are as a rule soluble in all the above solvents, while their salts are insoluble. If, therefore, we start with an acid aqueous solution of, say, quinine sulphate, and, having added sufficient alkali to set free the quinine, we shake up with chloroform, and then leave the latter to settle, the chloroformic layer will contain all the alkaloid. If we then run off this layer and shake it up with diluted sulphuric acid, the quinine will become quinine sulphate, and, being insoluble in the chloroform, will then leave that solvent, and pass to the aqueous layer once more in its original form. The main exception to these rules is morphine, which only comes out satisfactorily from its alkalised salts to warm amylic alcohol. If a drug should also contain resinous or other matters soluble in the chloroform, they will come into it with the free alkaloids, but will remain behind when the chloroformic solution is acted upon by acidulated water. The process is done in a separator (see fig. 17, p. 93), and the following precautions are so lucidly described by the U.S.P. that they cannot be improved upon:—

When the solution of an alkaloid, suitably prepared, is introduced into a separator, and chloroform subsequently added, the latter, owing to its higher specific gravity, will form the lower layer. If the two layers are violently shaken together, there will often result an emulsion, which will separate only slowly, and often imperfectly. This is particularly liable to happen when the aqueous liquid containing the alkaloid either in suspension or in solution is strongly alkaline, and when it has a high specific gravity. To avoid the formation of an emulsion, the extraction should be accomplished rather by rapid rotation and frequent inversion of the separator than by violent shaking. When an emulsion has formed, its separation may be promoted by the addition of more of the solvent, preferably somewhat heated, aided, if necessary, by the external application of a gentle heat (the stopper being removed for the time being), or by the introduction of a small quantity of alcohol or of hot water. The separation of the two layers may also be promoted by stirring the lower, chloroformic layer with a glass rod, and detaching from the walls of the separator the adhering drops of emulsion. On withdrawing the chloroform solution of an alkaloid from the separator, a small amount of the solution will generally be retained in the outlet tube by capillary attraction. If this were lost, the results of the assay would be seriously vitiated. To avoid this loss, several successive, small portions of chloroform should be poured into the separator without agitation, and drawn off through the stopcock to wash out the outlet tube. Another source of loss is the pressure sometimes generated in the separator by the rise of temperature caused when an alkaline and an acid liquid are shaken together. On loosening the stopper, the liquid which adheres to the juncture of the latter with the neck is liable to be ejected. This is best avoided by mixing the liquids at first by rotation (avoiding contact of the contents with the stopper), and allowing them to become cold before stoppering the separator. The same precautions should be observed when an alkali carbonate has been used, in place of a caustic alkali, for setting free the alkaloid. In this case the liquids should be cautiously and gradually mixed by rotation, and the separator should be left unstoppered until gas is no longer given off. If a regular glass separator is not available, and the quantity of liquid is small, an ordinary burette, stoppered with a sound cork, may be employed in its place.

III. ASSAY OF EXTRACT OF NUX VOMICA.

Extract of nux vomica, dried at 100° C (212° F.), *two grammes.*
Alcohol,
Ammonia water,
Water,
Chloroform,
Decinormal sulphuric acid V.S.,
Centinormal potassium hydrate V.S., each, *a sufficient quantity.*

Put 2 grammes of the dried extract of nux vomica into a glass separator, add to it 20 c.c. of a previously prepared mixture of 2 volumes of alcohol, 1 volume of ammonia water (0·960 sp. gr.) and 1 volume of water, and shake the well-stoppered separator until the extract is dissolved. Then add 20 c.c. of chloroform and agitate during five minutes. Allow the chloroform to separate, remove it as far as possible, pour into the separator a few c.c. of chloroform, and, without shaking, draw this off through the stopcock to wash the outlet tube. Repeat the extraction with two further portions of chloroform of 15 c.c. each, and wash the outlet tube each time as just directed. Collect all the chloroformic solutions in a wide beaker, expose the latter to a gentle heat, on a water bath, until the chloroform and ammonia are completely dissipated, add to the residue 10 c.c. of decinormal sulphuric acid measured with great care from a burette, stir gently, and then add 20 c.c. of hot water. When solution has taken place, add 2 c.c. of brazil-wood T.S., and then carefully run in centinormal potassium hydrate V.S., until a permanent pinkish colour is produced by the action of a slight excess of alkali upon the brazil-wood indicator. Divide the number of c.c. of centinormal potassium hydrate V.S. used by 10, subtract the number found from 10 (the 10 c.c. of decinormal acid used), multiply the remainder by 0·0364 and that product by 50 (or, multiply at once by 1·82), which will give the percentage of *total alkaloids* in the extract of nux vomica, it being assumed that strychnine and brucine are present in equal proportion, and the above factor being found by taking the mean of their respective molecular weights rounded off to whole numbers [(334 + 394) ÷ 2 = 364].

Extract of nux vomica, when assayed by the foregoing process, should be found to contain 15 per cent. of total alkaloids.

IV. ASSAY OF CINCHONA.

(*A*) For Total Alkaloids.

Cinchona, in No. 80 (or finer) powder, and completely dried at 100° C. (212° F.), *twenty grammes.*
Alcohol,
Ammonia water,
Chloroform,
Ether,
Normal sulphuric acid (V.S.),
Potassium hydrate V.S., each, *a sufficient quantity.*

To 20 grammes of cinchona, in very fine powder, and contained in a bottle provided with an accurately ground glass stopper, add 200 c.c. of a previously prepared mixture of 19 volumes of alcohol, 5 volumes of chloroform, and 1 volume of ammonia water, stopper the bottle, and shake it thoroughly and frequently during four hours. Then separate the liquid by pouring it into another bottle through a funnel containing a pellet of cotton, in such a manner that no material loss by evaporation may result. Transfer 100 c.c. of the clear filtrate (representing 10 grammes of cinchona) to a beaker, and evaporate it to dryness. Dissolve the residue of crude alkaloids thus obtained in 10 c.c. of water and 4 c.c. of normal sulphuric acid, with the aid of a gentle heat, filter the cooled solution into a separatory funnel, and wash the beaker and filter until the filtrate no longer has an acid reaction, using as small a quantity of water as possible. Now add 5 c.c. of potassium hydrate V.S., or such an amount as will render the liquid decidedly alkaline, and extract the alkaloids by shaking the mixture, first with 20 c.c., and then repeatedly with 10 c.c., of chloroform, until a drop of the last chloroform extraction, when evaporated on a watch-glass, no longer leaves a residue. Evaporate the united chloroformic extracts in a tared beaker, dry the residue at 100° C. (212° F.), and weigh. The weight found, multiplied by *ten* (10), will give the percentage of *total alkaloids* in the specimen of cinchona tested.

(*B*) For Quinine.

Transfer 50 c.c. of the clear filtrate remaining over from the preceding process (and representing 5 grammes of cinchona) to a beaker, evaporate it to dryness, and proceed as directed in the assay for total alkaloids, using, however, only one-half the amounts of volumetric acid and alkali there directed. Add the united chloroformic extracts containing the alkaloids in solution, gradually, and in small portions at a time, to about 5 grammes of powdered glass contained in a porcelain capsule placed over a water bath, so that, when the contents of the capsule are dry, all or nearly all of the dry alkaloids shall be in intimate admixture with the powdered glass, and the chloroform be completely expelled. Now moisten the residue with ether, and, having placed a funnel containing a filter of a diameter of 7 cm., and well wetted with ether, over a small graduated tube (A), transfer to the filter the ether-moistened residue from the capsule. Rinse the latter several times, if necessary, with fresh ether, so as to transfer the whole of the residue to the filter, then percolate with ether added drop by drop, until exactly 10 c.c. of percolate have been obtained. Then collect another volume of 10 c.c., by similar, slow percolation with ether, in a second graduated tube (B). Transfer the contents of the two tubes completely (using ether for washing) to two small, tared capsules, properly marked (A and B) so as to avoid confusion, evaporate to a constant weight at 100° C. (212° F.), and weigh them. (The residue in A will contain practically all the quinine, together with a portion of the alkaloids less soluble in ether; the residue in B will consist almost entirely of these alkaloids.) From the amount of residue obtained in capsule A deduct that contained in B, and multiply the remainder by *twenty* (20). The product will represent, approximately, the percentage of *quinine* (containing 1 molecule of water) in the specimen of cinchona tested.

V. ESTIMATION OF ALKALOIDS IN SCALE PREPARATIONS.

(*A*) Estimation of Quinine in Ferri et Quininæ Citras.

Dissolve 1·12 (1·1176) gramme of iron and quinine citrate in a capsule, with the aid of a gentle heat, in 20 c.c. of water. Transfer the solution, together with the rinsings of the capsule, to a separator, allow the liquid to become cold, then add 5 c.c. of ammonia water and 10 c.c. of chloroform, and shake. Allow the liquids to separate, draw off the chloroform layer, and shake the residuary liquid a second and a third time with 10 c.c. of chloroform. Allow the combined chloroformic extracts to evaporate spontaneously in a tared capsule, and dry the residue at a temperature of 100° C. (212° F.) to a constant weight. This residue should weigh not less than 0·1288 gramme (corresponding to at least 11·5 per cent. of dried quinine), and should conform to the reactions and tests of quinine.

(*B*) Estimation of Strychnine in Ferri et Strychninæ Citras.

Dissolve 2·24 (2·2352) grammes of iron and strychnine citrate in a separator in 15 c.c. of water, add 5 c.c. of ammonia water and 10 c.c of chloroform, and shake. Allow the liquids to separate, draw off the chloroform layer, and shake the residuary liquid a second and a third time with 10 c.c. of chloroform. Allow the combined chloroformic extracts to evaporate spontaneously in a tared capsule, and dry the residue at a temperature of 100° C. (212° F.) to a constant weight. This residue should weigh not less than 0·02 gramme nor more than 0·0224 gramme (corresponding to not less than 0·9 nor more than 1 per cent. of strychnine), and should respond to the reactions and tests of strychnine.

VI. ASSAY OF OPIUM.

Opium, in any condition to be valued, *ten grammes.*
Ammonia water, *three and five-tenths cubic centimetres.*
Alcohol,
Ether,
Water, each, *a sufficient quantity.*

Introduce the opium (which, if fresh, should be in very small pieces, and, if dry, in very fine powder) into a bottle having a capacity of about 300 c.c., add 100 c.c. of water, cork it well, and agitate frequently during twelve hours. Then pour the whole as evenly as possible upon a wetted filter having a diameter of 12 cm., and, when the liquid has drained off, wash the residue with water, carefully dropped upon the edges of the filter and the contents, until 150 c.c. of filtrate are obtained. Then carefully transfer the moist opium back to the bottle by means of a spatula, add 50 c.c. of water, agitate thoroughly and repeatedly during fifteen minutes, and return the whole to the filter. When the liquid has drained off, wash the residue, as before, until the second filtrate measures 150 c.c., and finally collect about 20 c.c. more of a third filtrate. Evaporate in a tared capsule, first, the second filtrate to a small volume, then add the first filtrate, rinsing the vessel with the third filtrate, and continue the evaporation until the residue weighs 14 grammes. Rotate the concentrated solution about in the capsule until the rings of extract are redissolved, pour the liquid into a tared Erlenmeyer flask having a capacity of about 100 c.c., and rinse the capsule with a few drops of water at a time, until the entire solution weighs 20 grammes. Then add 10 grammes (or 12·2 c.c.) of alcohol, shake well, add 25 c.c. of ether, and shake again. Now add the ammonia water from a graduated pipette or burette, stopper the flask with a sound cork, shake it thoroughly during ten minutes, and then set it aside, in a moderately cool place, for at least six hours, or over-night.

Remove the stopper carefully, and, should any crystals adhere to it, brush them into the flask. Place in a small funnel two rapidly acting filters of a diameter of 7 cm., plainly folded, one within the other (the triple fold of the inner filter being laid against the single side of the outer filter), wet them well with ether, and decant the ethereal solution as completely as possible upon the inner filter. Add 10 c.c. of ether to the contents of the flask, rotate it, and again decant the ethereal layer upon the inner filter. Repeat this operation with another portion of 10 c.c. of ether. Then pour into the filter the liquid in the flask, in portions, in such a way as to transfer the greater portion of the crystals to the filter, and, when this has passed through, transfer the remaining crystals to the filter by washing the flask with several portions of water, using not more than about 10 c.c. in all. Allow the double filter to drain, then apply water to the crystals, drop by drop, until they are practically free from mother-water, and afterwards wash them, drop by drop, from a pipette, with alcohol previously saturated with powdered morphine. When this has passed through, displace the remaining alcohol by ether, using about 10 c.c., or more if necessary. Allow the filter to dry in a moderately warm place, at a temperature not exceeding 60° C. (140° F.), until its weight remains constant, then carefully transfer the crystals to a tared watch-glass and weigh them.

The weight found, multiplied by 10, represents the percentage of crystallised morphine obtained from the opium.

VII. ASSAY OF EXTRACT OF OPIUM.

Extract of opium, dried at 100° C. (212° F.), *four grammes.*
Ammonia water, *two and two-tenths cubic centimetres.*
Alcohol,
Ether,
Water, each, *a sufficient quantity.*

Dissolve the extract of opium in 30 c.c. of water, filter the solution through a small filter, and wash the filter and residue with water, until all soluble matters are extracted, collecting the washings separately. Evaporate, in a tared capsule, first, the washings to a small volume, then add the first filtrate, and evaporate the whole to a weight of 10 grammes. Rotate the concentrated solution about in the capsule until the rings of extract are redissolved, pour the liquid into a tared Erlenmeyer flask having a capacity of about 100 c.c., and rinse the capsule with a few drops of water at a time, until the entire solution weighs 15 grammes. Then add 7 grammes (or 8·5 c.c.) of alcohol, shake well, add 20 c.c. of ether, and shake again. Now add the ammonia water from a graduated pipette or burette, stopper the flask with a sound cork, shake it thoroughly during ten minutes, and then set it aside, in a moderately cool place, for at least six hours, or over-night.

Remove the stopper carefully, and, should any crystals adhere to it, brush them into the flask. Place in a small funnel two rapidly acting filters, of a diameter of 7 cm., plainly folded, one within the other (the triple fold of the inner filter being laid against the single side of the outer filter), wet them well with ether, and decant the ethereal solution as completely as possible upon the inner filter. Add 10 c.c. of ether to the contents of the flask, rotate it, and again decant the ethereal layer upon the inner filter. Repeat this operation with another portion of 10 c.c. of ether. Then pour into the filter the liquid in the flask, in portions, in such a way as to transfer the greater portion of the crystals to the filter, and, when this has passed through, transfer the remaining crystals to the filter by washing the flask with several portions of water, using not more than about 10 c.c. in all. Allow the double filter to drain, then apply water to the crystals, drop by drop, until they are practically free from mother-water, and afterwards wash them, drop by drop, from a pipette, with alcohol previously saturated with powdered morphine. When this has passed through, displace the remaining alcohol by ether, using about 10 c.c., or more if necessary. Allow the filter to dry in a moderately warm place, at a temperature not exceeding 60° C. (140° F.), until its weight remains constant, then carefully transfer the crystals to a tared watch-glass and weigh them.

The weight found, multiplied by 25, represents the amount of crystallised morphine obtained from 100 grammes of the extract.

VIII. ASSAY OF TINCTURE OF OPIUM.

Tincture of opium, *one hundred cubic centimetres.*
Ammonia water, *three and five-tenths cubic centimetres.*
Alcohol,
Ether,
Water, each, *a sufficient quantity.*

Evaporate the tincture to about 20 c.c., add 40 c.c. of water, mix thoroughly, and set the liquid aside for an hour, occasionally stirring, and disintegrating the resinous flakes adhering to the capsule. Then filter, and wash the filter and residue with water, until all soluble matters are extracted, collecting the washings separately. Evaporate in a tared capsule, first, the washings to a small volume, then add the first filtrate, and evaporate the whole to a weight of 14 grammes. Rotate the concentrated solution about in the capsule until the rings of extract are redissolved, pour the liquid into a tared Erlenmeyer flask having a capacity of about 100 c.c., and rinse the capsule with a few drops of water at a time, until the entire solution weighs 20 grammes. Then add 10 grammes (or 12·2 c.c.) of alcohol, shake well, add 25 c.c. of ether, and shake again. Now add the ammonia water from a graduated pipette or burette, stopper the flask with a sound cork, shake it thoroughly during ten minutes, and then set it aside, in a moderately cool place, for at least six hours, or over-night.

Remove the stopper carefully, and, should any crystals adhere to it, brush them into the flask. Place in a small funnel two rapidly acting filters, of a diameter of 7 cm., plainly folded, one within the other (the triple fold of the inner filter being laid against the single side of the outer filter), wet them well with ether, and decant the ethereal solution as completely as possible upon the inner filter. Add 10 c.c. of ether to the contents of the flask, rotate it, and again decant the ethereal layer upon the inner filter. Repeat this operation with another portion of 10 c.c. of ether. Then pour into the filter the liquid in the flask, in portions in such a way as to transfer the greater portion of the crystals to the filter, and, when this has passed through, transfer the remaining crystals to the filter by washing the flask with several portions of water, using not more than about 10 c.c. in all. Allow the double filter to drain, then apply water to the crystals, drop by drop, until they are practically free from mother-water, and afterwards wash them, drop by drop, from a pipette, with alcohol previously saturated with powdered morphine. When this has passed through, displace the remaining alcohol by ether, using about 10 c.c., or more if necessary. Allow the filter to dry in a moderately warm place, at a temperature not exceeding 60° C. (140° F.), until its weight remains constant, then carefully transfer the crystals to a tared watch-glass and weigh them.

The weight found represents the amount of crystallised morphine obtained from 100 c.c. of the tincture.

If 100 c.c. of tincture of opium be assayed by the above process, it should yield from 1·3 to 1·5 gramme of crystallised morphine.

IX. ESTIMATION OF THE STRENGTH OF RESINOUS DRUGS.

Take 5 to 10 grammes of the drug in powder, and place it in a strong glass flask with 100 c.c. of rectified spirit. Close the flask with a good cork, and digest it in a warm place at about 50° C. for twelve hours, shaking from time to time. Pour or filter off 80 c.c. (representing $\frac{8}{10}$ of the total drug taken), place it in a weighed beaker, and evaporate to 25 c.c. on the top of the water bath. Now add 50 c.c. of distilled water, and boil gently over a low gas flame till all the alcohol is driven off. Let it cool and perfectly settle, pour off the supernatant liquor, wash the deposited resin by decantation with hot distilled water, and then dry the beaker and its contents in the air bath at 105° C. and weigh, deducting the tare of the beaker. Thus treated, jalap, for example, should show from 9 to 11 per cent. of resin, of which not more than one-tenth should be soluble in ether. Scammonium, on the other hand, should yield 70 per cent. of resin, entirely soluble in ether, and also in solution of potash, from which latter it is not re-precipitated by excess of diluted HCl.

X. EXAMINATION OF A TINCTURE OR OTHER ALCOHOLIC LIQUOR FOR THE PRESENCE OF METHYLATED SPIRIT.

The alcoholic liquors are first to be distilled until a part of the spirit has passed over and the distillate treated as follows:—

About 3 c.c. is placed in a small flask fitted with a cork and a tube having two rectangular bends, with one end dipping into a test tube kept cold by immersion in water, and to the flask are added 3 grammes of potassium bichromate and 2·5 c.c. of sulphuric acid diluted with 20 c.c. distilled water. The mixture, after standing for twenty minutes, is distilled at a gentle heat, until nearly the whole has passed over. Sodium carbonate having been added to the distillate till it is slightly alkaline, the liquid is evaporated in a porcelain basin to about half its bulk, and, having been acidulated slightly by acetic acid, is transferred to a test tube, heated gently with twenty drops of a 5 per cent. solution of argentic nitrate for a few minutes, when any decided opacity (due to the discoloration of the fluid, and the separation of a blackish precipitate of metallic silver) indicates the presence of methyl alcohol in the sample thus tested. In the oxidation of ordinary alcohol, a trace of formic acid is formed by secondary decomposition ; consequently *a distinct precipitate must be obtained before the spirit can, with certainty, be pronounced to be methylated.*

When this process has to be applied to sweet spirit of nitre, the ethyl nitrite must be first got rid of, as follows :

Take a little of the spirit and place it in a bottle with some dry potassium carbonate, and shake up Let it settle, and take about two drachms of the strong spirit which separates. Saturate this with calcium chloride, and distil on a water bath, rejecting the distillate (ethyl nitrite, etc.). Add a little water to the contents of the retort and distil again, when the pure spirit will come over, and a portion may then be tested as above directed. Really it is the most simple thing to saturate the strong spirit with the calcium chloride in a little basin, and then to put it on the water bath until all odour of nitrous ether ceases to be evolved, and then to add the water and wash into the distilling flask.

XI. ANALYSIS OF FIXED OILS AND FATS.

This is a matter requiring the greatest practice and experience, and, unfortunately, it is still possible so to sophisticate dear with cheaper oils as to practically defy definite analysis. If, however, we confine our attention to the ordinary fixed oils of the B P., we can get a very fair idea of their purity, or otherwise, by applying the following methods :—

(1) **Specific Gravity**. (*a*) *In the case of oils*, this is to be taken in the usual way at 15·5 C. The average gravities of the common oils are —

Almond	·915 to ·920.
Castor	·950 .. ·970.
Cod liver	·920 .. ·925.
Cotton (a common adulterant)	·922 .. ·929.
Linseed	·930 .. ·940.
Olive	·915 .. ·918.

(*b*) *In the case of solid fats*, we melt them, and take their gravity either at 38° C. or at the boiling point of water. For a person not continually operating with oils, the latter is the more likely to give good results, and may be worked in the following manner

Take an ordinary specific-gravity bottle with a well-fitting *perforated* stopper, and also a deep basin capable of holding a good deal more water than will quite cover the bottle. Charge the basin with distilled water, and put it over a good gas flame, so that it is rapidly heated to boiling point.

Melt the fat, and charge the specific-gravity bottle with it in the usual way, and then, holding it with a pair of wooden tongs, plunge it into the water so that it lies on its side, entirely immersed, with its neck pointing downwards. The melted fat expands, and, passing through the hole in the stopper, absolutely prevents the entrance of any of the water, which must be *kept briskly boiling for twenty minutes*. The bottle is then fished out, rapidly wiped dry, cooled, and weighed. The weight of the empty bottle having been deducted, the balance gives the weight of fat it holds at the temperature of boiling water, which, divided by the weight of water that the bottle holds under the same conditions, gives a sufficiently accurate gravity for all ordinary purposes. Thus treated the following solid fats give—

Butter	·867 to ·870.
Lard	·860 .. ·861.
Cacao butter	·857 .. ·858.
Beef fat	·857 .. ·859.

(2) **Hubl's Method of Iodine Absorption.** *Solutions*, etc., required:—

(1) A solution of 25 grammes of iodine and 30 grammes of mercuric chloride, each dissolved in 500 c.c. of B.P. absolute alcohol, and the latter added to the former. The mixing is to be done twelve hours before use. This is called "Hubl's" reagent.
(2) A volumetric solution of sodium thiosulphate, made by diluting the ordinary B.P. solution with an equal bulk of water, and then standardising against decinormal solution of iodine, so that 2 c.c. of the "hypo" corresponds to 1 c.c. of the iodine, and therefore represents ·00635 of iodine.
(3) A light stoppered flask of known weight, capable of holding about 50 c.c.
(4) An ordinary stoppered 12-oz. bottle.
(5) Pure chloroform.
(6) Thin starch mucilage.

The oil or melted fat is first weighed into the stoppered flask, taking under ·3 gramme of linseed, cod-liver, or any "drying" or fish oil, under ·4 gramme of olive or almond, and under ·8 gramme of lard or other solid fat. To this is added 10 c.c. of chloroform and 25 c.c. of the "Hubl" solution. If the liquid is now turbid, another few c.cs. of chloroform must be added till it is quite clear. It is then stoppered, and put away in a dark place for at least eight hours. At the same time a similar flask is charged with 25 c.c. of "Hubl," and the same volume of chloroform as employed in the former case, and put away with it. At the end of the time 20 c.c. of a 10 per cent. solution of potassium iodide are added to the flask containing the oil; the whole is then transferred to a 12-oz. bottle, and, with the rinsings, made up to 150 c.c. with distilled water. It is then titrated with "hypo" in the usual way, closing the bottle after each addition and shaking violently, so as to act on the iodine dissolved in the chloroformic layer at the bottom. The other flask, containing the check experiment, is treated in exactly the same way, and the difference between the volumes of "hypo" used in the two experiments is calculated to the iodine it represents, and the result calculated to percentage from the weight of oil started with. The important point to be observed is that there must be a large excess of iodine over that actually required, so that, after standing, the contents of the flask do not seem to be much lighter in colour than at starting. Thus treated, the oils and fats referred to above show:—

	Per cent. of iodine absorbed.		
Almond	98	to	99.
Castor	84	,,	84·5.
Cod liver	158·7	,,	166·6.
Cotton	106	,,	110.
Linseed	173	,,	187.
Olive	79	,,	80·9.
Lard	52	,,	62·5.
Beef fat	34	,,	45.

(3) **Saponification Equivalent** (Kœttstorfer's process). *Solutions*, etc., required:—

(1) A solution of 28 grammes of pure potassium hydrate in 1 litre of B.P. absolute alcohol.
(2) Accurate seminormal hydrochloric acid (18·25 grammes real HCl per litre).
(3) A strong glass flask, holding 100 c.c., capable of standing pressure, and furnished with a good cork.

The flask is counterbalanced, 2·5 grammes of the oil or melted fat are weighed into it, and 25 c.c. of the potash solution are very accurately added from a delicate burette. The flask is closed, placed on the top of the water oven, occasionally rotated until all the fat is completely dissolved and saponified. A little alcoholic solution of phenol-phthalein having been added, the whole is titrated with the acid until just colourless. At the same time a blank experiment on another 25 c.c. of the potash is made side by side, and the difference between the two titrations is calculated to KHO by multiplying the number of c.c. of difference by ·028, and then calculating to percentage This is, however, sometimes expressed also as a "saponification equivalent," by dividing the weight of fat taken, *expressed in milligrammes* by *half* the number of c.c. of acid found as the difference between the two experiments. Thus treated, the fats and oils already mentioned show :—

	Per cent. of KHO neutralised.
Almond	19·5.
Castor	17·71 to 18·02.
Cod liver	18·51 ,, 18·52.
Cotton	19·09 ,, 19·35.
Linseed	19·00 ,, 19·28.
Olive	18·00 ,, 19·20.
Lard	19·20 ,, 19·60.
Cacao butter	19·32 ,, 19·80.
Beef fat	19·80 ,, 19·98.

(4) **Specific Heating Power**. The process consists in placing 50 grammes of the oil or melted fat in a glass cylinder, immersing a thermometer, noting the temperature, and then causing 10 c.c. of strong sulphuric acid, brought to exactly the same temperature as that of the oil, to flow slowly in from a stoppered burette, stirring with the thermometer all the time, and noting the extreme point to which the mercury rises. The experiment is then repeated *under exactly the same conditions*, using 50 c.c. of distilled water instead of oil, and the rise is again noted. Lastly, the rise in temperature observed with the oil is divided by that shown with the water. The stopper of the burette should be so set that it takes exactly one minute to deliver 10 c.c. of acid. The following are some characteristic results :

Water	1·00.
Castor	·89 to ·92.
Cod liver	2·46 ,, 2·72.
Cotton	1·63 ,, 1·70
Linseed	3·20 ,, 3·49.
Olive	·89 ,, ·94

The rise is so great with linseed oil, that it is best to work upon it after diluting it *one half* with a mineral oil, previously found to give only a slight definite rise, and to make a correction.

(5) Some Useful Qualitative Tests for Oils and Fats as employed by the U.S.P.

(*a*) *For Cotton Seed Oil or Fats in Olive Oil and Lard* (Becchi's test). To 5 grammes of the oil or melted fat in a tube add 5 c.c. of a 1 per cent solution of $AgNO_3$ in *pure* alcohol of 92 per cent. (deodorised alcohol U.S.P.), add one drop of strong nitric acid, shake thoroughly, and place the tube in boiling water for 5 to 10 minutes, shaking at intervals. If pure, no reddish or brownish tint should be produced in the oily layer, nor should any dark colour be produced at the line of contact of the liquids.

(*b*) *Test for Sesame Oil* If 5 c.c. of the oil be shaken with an equal volume of concentrated hydrochloric acid, the latter will usually assume a bright emerald green colour, especially if the oil has been exposed for some time to the action of air and light, and, on the subsequent addition of about 0·5 gramme of sugar, and again shaking the mixture, a blue colour, changing to violet, and finally to deep crimson, will be produced. This test is due to the production and action of *furfurol*, and many analysts prefer to use a 1 per cent solution of furfurol in spirit instead of the sugar When it is desired to detect sesame oil in other oils or fats, about 30 c.c. of the oil should be saponified by 20 c.c. of 25 per cent. alcoholic solution of potassium hydrate, then diluted with 200 c.c. of water, and freed from alcohol by boiling. On then supersaturating the solution with diluted sulphuric acid, the fatty acids will form a layer on the surface, and these having been separated as far as possible, free from water, and filtered, 5 c.c. of the clear filtrate is taken for the furfurol test as above.

(*c*) *Tests for other Oils in Castor Oil.* (1) If 3 c.c. of the oil be shaken for a few minutes with 3 c.c. of carbon disulphide and 1 c.c. of sulphuric acid, the mixture should not acquire a blackish-brown colour.

(2) Soluble in an equal volume of alcohol of ·820 sp. gr. at 15·5° C., and, in all proportions, in absolute alcohol, or in glacial acetic acid; also soluble, at 15° C. (59° F.), in three times its volume of a mixture of 19 volumes of alcohol of ·820 sp. gr. at 15·5° C. and 1 volume of water (absence of more than about 5 per cent. of *most other fixed oils*).

(*d*) *Tests for Purity of Almond Oil.* If 2 c.c. of the oil be vigorously shaken with 1 c.c. of fuming nitric acid and 1 c.c. of water, a whitish (not red or brownish) mixture should be formed, which, after standing for some hours at about 10° C. (50° F.), should separate into a solid, white mass, and a scarcely coloured liquid (distinction from the fixed oils of *apricot* and *peach kernels*, and from *sesame*, *cotton-seed*, and *poppy-seed oils*).

If 10 c.c. of the oil be mixed with 15 c.c. of a 15 per cent. solution of sodium hydrate and 10 c.c. of alcohol, and the mixture allowed to stand at a temperature of 35° to 40° C. (95° to 104° F.), with occasional agitation, until it becomes clear, and then diluted with 100 c.c. of water, the clear solution thus obtained, upon the subsequent addition of an excess of hydrochloric acid, will set free a layer of oleic acid. This, when separated from the aqueous liquid, washed with warm water, and clarified on a water bath, will remain liquid at 15° C. (59° F.), although sometimes depositing particles of solid matter and becoming turbid. One part of this oleic acid, when mixed with 1 volume of alcohol of ·820 sp. gr., should give a clear solution, which at 15° C. (59° F.) should not deposit any fatty acids, nor become turbid on the further addition of 1 volume of alcohol (distinction from *olive*, *arachis*, *cotton-seed*, *sesame*, and *other fixed oils*).

(*e*) *Tests for the Purity of Linseed Oil.* If 2 c.c. of the oil be shaken with 1 c.c. of fuming nitric acid and 1 c.c. of water, it should neither completely nor partially solidify, even after standing for one or two days (absence of *non-drying oils*).

If 10 c.c. of the oil, contained in a small flask, be mixed with a solution of 3 grammes of potassium hydrate in 5 c.c. of water, then 5 c.c. of alcohol added, and the mixture heated for about five minutes on a water bath, with occasional agitation, a dark-coloured but clear and complete solution should be obtained. If this liquid be diluted with water to the measure of 50 c.c., then cooled, and shaken with 50 c.c. of ether, the clear, ethereal layer, after having separated, should not show a bluish fluorescence, and, when carefully decanted, and allowed to evaporate spontaneously, should leave not more than a slight, and not oily, residue (absence of *paraffin oils*).

(*f*) *Tests for Purity of Oil of Theobroma.* If 1 gramme of oil of theobroma be dissolved in 3 c.c. of ether, in a test tube, at a temperature of 17° C. (63° F.), and the tube subsequently plunged into water at 0 C. (32° F.), the liquid should not become turbid, nor deposit a granular mass in less than three minutes; and if the mixture, after congealing, be exposed to a temperature of 15° C. (59° F.), it should gradually form a perfectly clear liquid (absence of *paraffin*, *wax*, *stearin*, *tallow*, etc.).

(6) Mineral Oil, Soft Paraffin, or other Unsaponifiable Matters in Fats. Ten grammes of the fat may be saponified with 50 c.c. of normal alcoholic potash (5·6 per cent.), as directed above (§ 3). The alcoholic liquid is diluted with water, and some sodium bicarbonate having been added (to convert the excess of caustic alkali into carbonate), the whole is poured into a basin, into which some clean sand has been previously placed, and evaporated to dryness over the water bath, stirring well towards the end of the process. The dry residue is then scraped off the basin into a dry bottle, and 200 c.c. of ether (or petroleum spirit) having been added, the bottle is closed and shaken from time to time, and then set aside for twelve hours to settle. 100 c.c. are poured off clear into a weighed basin, and the solvent being driven off by a gentle heat, the residue of mineral oil, paraffin, or unsaponifiable matter is weighed. All fats contain some small trace of unsaponifiable matter, but mineral oil or soft paraffin are easily recognised by their characters when thus isolated.

(7) **Free Acids in Fats.** If some phenol-phthalein be added to rectified spirit, and then exceedingly dilute soda added drop by drop till a faint pink is produced, and the oil or fat be introduced, and the whole warmed and shaken, the colour will disappear in the presence of any free acid. To estimate its amount a weighed quantity is treated in the same way, and titrated with decinormal soda till the pink is restored. Each c.c. of $\frac{n}{10}$ soda = ·0282 oleic acid or ·0284 of stearic acid. The B.P. employs this method to find that the free fatty acids in wool fat are not excessive. It takes 50 grains, dissolves in ether, adds phenol-phthalein, and uses two grain measures of *normal* soda.

(8) **Estimation of Oleic Acid.** One gramme of the impure fatty acid is saponified in a basin by heating with a slight excess of alcoholic potash till dissolved, and then diluted with water. This solution is treated with acetic acid drop by drop, until on stirring a faint *permanent* turbidity ensues. Dilute solution of potassium hydrate is then stirred in drop by drop till the liquid just clears up, and then solution of plumbic acetate is stirred in until precipitation ceases. The precipitate having been allowed to settle, the supernatant liquor is poured off and the soap washed once with boiling water. A little clean sand is rubbed up with the soap in the basin, and the whole scraped out and transferred to a "Soxhlet," in which it is thoroughly exhausted with 90 c.c. of *pure* ether. The ethereal solution (which now contains only plumbic oleate, the plumbic palmitate and stearate being left insoluble in the "Soxhlet") is transferred to a special apparatus, sold by apparatus vendors as "Muter's oleine tube." This is a graduated and stoppered tube holding 120 c.c., and having a spout and stopcock at 30 c.c. from its base. Previously to introducing the ether, place 20 c.c. of dilute hydrochloric acid (1 in 3) into the tube, and then make up the whole with ether rinsings of the basin to the 120 c.c. mark. Close the tube, shake well, and set aside. When settled, note the full volume of the ethereal solution of oleic acid, and run off an aliquot part from the tap into a weighed dish, evaporate, dry in the water oven, and weigh. Finally calculate this weight to that of the whole bulk of ethereal solution previously noted, thus getting the amount of real oleic acid present in the gramme of crude acid started with.

(9) **Detection and Estimation of Arachidic Acid.** This becomes necessary when it is desired to detect the presence of *ground-nut oil* in olive or other seed oils. The grammes of the oil are treated exactly as above directed for the estimation of oleic acid up to the point of extraction with ether. The residue left in the "Soxhlet" contains plumbic arachidate if ground-nut oil be present. This residue is suspended in hot water and acidulated with HCl, when the free fatty acids float to the top and form a cake on cooling. This cake is dissolved by heat in 50 c.c. of 90 per cent. alcohol, and on cooling

any arachidic acid is deposited in crystals. Filter these crystals off, and wash them on the filter, first with a *limited and measured* number of c.c. of 90 per cent. alcohol at 20° C., then with 70 per cent. alcohol, and finally dissolve them by pouring boiling absolute alcohol on the filter, receiving the filtrate in a tared dish or flask. Evaporate to dryness on the water bath, and weigh the residue, consisting of crude arachidic acid. Add to the weight thus obtained ·000045 for each c.c. of the 90 per cent. alcohol used (that being the solubility of arachidic acid in such alcohol at 20° C.). Finally the amount of ground-nut oil present in the sample may be found by multiplying the weight of the acid by 20.

(10) **Estimation of Rosin Oil in Fats.** This process depends upon the fact that, when an ordinary oil is acted upon by bromine in the dark, little or no substitution of bromine for hydrogen takes place, and consequently there is only a very small production of hydrobromic acid, while with rosin oil and resin itself all the action is one of substitution, and, consequently, each molecule of hydrobromic acid formed must represent an atom of substituted bromine.

0·5 gramme of the oil is dissolved in a little carbon tetrachloride, and placed in a 500 c.c. bottle with an accurately ground stopper. To this is then added half a c.c. of bromine dissolved in 50 c.c. of carbon tetrachloride, and the whole is put away in the dark for eighteen hours. The bottle is then placed in ice, and a short piece of india-rubber tubing having been slipped over the neck, so as to form a well round the stopper, this receptacle is filled with distilled water, and the stopper is carefully opened, so that the water is sucked into the bottle without loss of hydrobromic acid vapour. The introduction of water is continued until 25 c.c. have been run in, and the bottle is then well shaken. Some potassium iodide having been added, with 75 c.c. more water and some starch water as an indicator, just sufficient solution of sodium thiosulphate is added until all colour is entirely removed. The contents of the bottle are then transferred to a separator, and the aqueous portion is run therefrom (through a filter if necessary) into a white basin and titrated with $\frac{N}{10}$ NaHO, using methyl orange as the indicator. The number of c.cs. of soda used, multiplied by 1·6 (*i.e.*, ·008 × 200), gives the "bromine substitution figure." For rosin oil this figure averages 57·5, consequently each ·575 of "bromine substitution" represents 1 per cent. of rosin oil in the sample. For linseed oil the results will be found very accurate, but, when dealing with oils generally, it is well to allow something for slight natural substitution, and it is therefore wise to overlook any "bromine substitution" obtained under 1 per cent. If the blue colour should return during the separation and filtration of the aqueous liquid, more thiosulphate is to be added before titration. The titration is more delicate when a measured excess of $\frac{N}{10}$ soda is added and then checked back with $\frac{N}{10}$ HCl.

XII. ANALYSIS OF WAXES.

I. **Bees' Wax.** (*a*) APPARATUS REQUIRED.

(1) A solution of 30 grammes KHO in 1000 c.c. alcohol of 90 per cent.
(2) Seminormal solution of HCl (= 18·25 grammes real HCl per litre).
(3) A flask of 250 c.c. capacity, heated by a water bath.
(4) An upright reflux condenser, having a cork to fit the flask.
(5) An alcoholic solution of phenol-phthalein which has been carefully treated with very dilute KHO until a *very faint* pink has been produced.

(*b*) THE PROCESS. Place 2·5 to 5·0 grammes of the wax into the flask with 50 c.c. of 90 per cent. alcohol, add some phenol-phthalein solution, heat to boiling, titrate with the alcoholic potash until a pink colour is developed, and record the number of c.c. of potash solution used as *titration No.* 1. Now continue the addition of the potash into the flask until 50 c.c. in all has been run in from the burette, attach the condenser and boil for an hour, during which the wax will saponify and dissolve; but should it contain paraffin, this latter will remain unaffected in greasy drops, frequently adhering to the flask. When the boiling is completed, detach the flask, estimate the excess of potash remaining uncombined by titration with $\frac{N}{2}$ HCl, till the pink colour is discharged, and note the number of c.c. used as *titration No. 2.* While the saponification of the wax is proceeding, the exact strength of the alcoholic potash is ascertained by titrating 50 c.c. with the $\frac{N}{2}$ HCl in the presence of phenol-phthalein, and noting the number of c.c. of the acid equivalent thereto. The volume of potash solution used in titration No. 1 is first calculated to the volume of $\frac{N}{2}$ HCl equivalent, and then the number of c.c. so found × $\frac{20 \cdot 5}{\text{weight of wax taken}}$ = percentage of CEROTIC ACID. Next take the volume of acid found to be equal to 50 c.c. of potash, and from that deduct the volume of acid employed in titration No. 2, when the difference in c.c. × $\frac{33 \cdot 8}{\text{weight of wax taken}}$ = percentage of MYRICINE (*myricyl palmitate*). Owing to the presence in all bees' wax of a little cerolein (having a lower equivalent than myricine), these two results will always add up to a trifle over 100 in the pure article.

(*c*) JUDGING THE RESULTS. Before forming an opinion it is necessary to test the wax qualitatively as follows:—

(1) *For fatty acid and resin*, by boiling 1 part of wax with 20 of alcohol, and filtering a portion into an excess of water, when pure wax will give only a slight opalescence, but fatty acid will separate in flocculent masses—and resin as a finely divided precipitate. The rest of the alcoholic liquid is to be then evaporated to dryness, and the residue, having been boiled with nitric acid (1·20 sp. gr.) and cooled, is treated with excess of solution of ammonia, when a blood red = resin.

(2) *For fats and Japan wax.* The residue of the wax insoluble in spirit is boiled with 35 c.c. of 15 per cent. aqueous solution of NaHO for half an hour (taking care to maintain the volume by occasional addition of water), cooled, filtered, and the filtrate acidulated with hydrochloric acid, when only a faint opalescence will occur with genuine wax.

(3) *For paraffin.* The presence of this body is generally sufficiently evident during saponification as above described. The following is the U.S.P. test, which is, unfortunately, not always successful with the kind of paraffin now used for adulterating bees' wax: If 5 grammes of yellow wax be heated in a flask for fifteen minutes, with 25 c.c. of sulphuric acid, to 100° C. (320° F.), and the mixture then diluted with water, no solid, wax like body should separate.

Having thus got the needful information, the principles on which we then calculate (laid down by Mr. Hehner, the inventor of the process, and subsequently confirmed by other observers) are as follows:—

(*a*) In genuine bees' wax the proportion of the two main constituents, when estimated as above, always comes out as 1 of cerotic to 6·117 of myricine (or practically 1 to 6).

(*b*) The presence of fatty acids increases the apparent percentage of cerotic acid, and the excess thus shown over the normal amount, calculated from the percentage of myricine found ÷ 1·518 = the fatty acid present.

(*c*) The presence of fat or Japan wax increases the apparent percentage of myricine, and such excess over the calculated normal amount of myricine ÷ 2·39 = fat present (or 2·52 = Japan wax).

(*d*) The presence of paraffin lowers both the cerotic acid and myricine in proportion, and its amount may be fairly obtained by adding them together and deducting from 100.

(*e*) When both fat and fatty acids or Japan wax (which contains free palmitic acid and palmitine, in the average proportion of about 1 to 10) are present, then it becomes a matter of algebra, and we apply the following formula, in which A = per cent. of apparent cerotic acid, B = per cent. of apparent myricine, X = unknown cerotic acid. Then—

$$X + \frac{A - X}{1{\cdot}518} + 6{\cdot}117X + \frac{B - 6{\cdot}117X}{2{\cdot}39} = 100, \text{ or}$$

$$X = 25{\cdot}649 - ({\cdot}1689A + {\cdot}1073B);$$

or for Japan wax—

$$X + \frac{A - X}{1{\cdot}601} + 6{\cdot}1X + \frac{B - 6{\cdot}1X}{2{\cdot}516} = 100.$$

Should such wax also contain paraffin, a direct estimation thereof must also be attempted. This may usually be done by destroying the wax on the water bath with fuming sulphuric acid, and then cooling, diluting, extracting the paraffin with ether or petroleum spirit, evaporating off the solvent, and weighing the paraffin. It is to be noted that an adulterant containing paraffin called "cerosin" is now produced, which sometimes defeats this process.

(*f*) No wax containing any notable amount of paraffin ever yields percentage of the two chief ingredients coming up to 100; while samples adulterated with fat and fatty acids (or Japan wax), and free from paraffin, always add up to a figure markedly exceeding 103.

II. Tests to distinguish between Chief Unofficial Waxes. Dissolve, by heat, 1 of wax in 10 of chloroform, and cool to 15° C.

Case I. The cold solution is clear.

- (1) The original is soluble in ether.
  - (*a*) Alcoholic Fe_2Cl_6 gives ppt. insoluble on boiling: *Myrica quercifolia.*
  - (*b*) Alcoholic Fe_2Cl_6 gives black: *Myrica* (species uncertain).
  - (*c*) " " " brown colour, but no ppt.: *Orizaba wax.*
- (2) The original is not entirely soluble in ether.
  Saponify by boiling with 10 parts of N alcoholic potash, and then boil with 100 parts H_2O:—
  - (*a*) Completely soluble: *Japan wax.*
  - (*b*) Only partially soluble: *African bees' wax.*

Case II. The cold chloroformic solution is turbid.

- (1) An alcoholic solution of the original becomes turbid with alcoholic plumbic acetate: *Lac wax.*
- (2) No turbidity is produced; then—
  - (*a*) An ethereal solution of the original mixed with its own volume of alcohol becomes turbid: *Carnauba wax.*
  - (*b*) The solution is clear: *Bahia wax.*

XIII. ANALYSIS OF SOAP.

(1) **Direct Estimation of Fatty Acids.** Two grammes of the soap, in fine shavings, are shaken up in a separator, with a slight excess of dilute sulphuric acid to liberate the acids. Ether is then added, and the fatty acids which have been liberated are dissolved up in it. When the decomposition of the soap is complete, the liquid below the ethereal solution is removed. With a little care this can be done very completely, without any loss of

the ethereal solution. The ether is then shaken up with distilled water, and the latter drawn off as before, and this process of washing repeated three times more. When all but a few drops of the wash-water has been drawn off, a few drops of barium chloride solution are added, the mixture shaken up, and the last traces of sulphuric acid thus removed. With a little practice so little water is left below the ethereal solution that the latter can be directly drawn off and evaporated in a weighed dish, and the residue finally dried in the water oven and weighed. The fatty acids thus obtained also contain resin acids in any soap made from fat and resin (such as *primrose* soap). In this case we must proceed to estimate the resin acids (sec. 5), and deduct them, when the balance will be the true fatty acids.

(2) **Convenient Method for General Analysis.** (*a*) Cut the soap across, and drop a solution of phenol-phthalein in alcohol upon the freshly cut surface, when any red colour shows the presence of free alkali. If free alkali be found, dissolve 5 grammes in absolute alcohol, add phenol-phthalein, titrate with decinormal acid, and calculate to NaHO or KHO, according to which alkali is present.

(*b*) Dissolve 2 grammes of the soap in absolute alcohol by the aid of heat, add a drop of solution of phenol phthalein, and pass CO_2 till any red colour disappears. Filter through a tared filter, and wash any insoluble matter found with warm alcohol, dry at 100° C., and weigh; this will give *total impurities* (such as alkaline carbonates, silicates, or borax). The filtrate and washings are then to be evaporated on the water bath in a weighed platinum dish, the residue being dried in the water oven to constant weight and weighed = actual *real* soap present. The dish and contents are then gently heated to redness, the residue left being dissolved in water and titrated with decinormal acid, using methyl orange as the indicator. The number of c.c. used is multiplied by ·0031 for hard soda soaps, or by ·0047 for soft potash soaps, and the resulting amount of alkali being deducted from the weight of real soap found, the difference × 1·03 = amount of fatty acids. The weights of *real* soap and *total impurities* added together, and deducted from 2, give the water present in the sample. Finally, everything is calculated to percentage.

(3) **Glycerine and Sugar in Soap.** The liquid run off from the separator during the estimation of the fatty acids (see par. 1) is neutralised with soda, and evaporated to dryness at a very gentle heat. The residue is extracted with a liquid composed of two parts, by volume, of absolute alcohol, and one of chloroform, filtered and washed with the same solvent. The filtrate is mixed with double its volume of distilled water, when the chloroform separates out, leaving the glycerine in the diluted spirit, in which it may be detected by the borax test, and estimated if desired by the author's copper process, originally published in "The Analyst," vol. vi., p. 41. The residue on the filter is dissolved in water, a few drops of the solution are tested for sugar, and, if it be found, the rest is inverted by dilute acid made to a fixed bulk, and the sugar estimated by Fehling. Sugar is a common adulterant of so-called "glycerine toilet soaps."

(4) **Carbolic Soaps.** Twenty grammes of the soap are dissolved in 20 c.c. of 10 per cent. solution of potash and 150 c.c. of water, and then 200 c.c. of brine (saturated) are added. This causes the soap to precipitate, and then 200 c.c. (equal to 10 grammes of soap) are filtered off, and evaporated until salt begins to separate out. The whole is then introduced into a specially shaped tube, known as "Muter's carbolic tube," and acidulated, when the carbolic or cresylic acids (phenols) rise to the top, and their amount is read off on a scale specially graduated for the purpose. This process is the only

one that will give a fair approximation to the phenols put in, the ordinary bromine method entirely failing unless pure crystallisable phenol has been used, which is rarely the case in ordinary cheap articles.

(5) **Estimation of Resin in Soap.** Ten grammes of the soap are dissolved in warm water, heated to boiling, and the fatty acids thrown up by excess of hydrochloric acid. The acids are collected, and washed with boiling water until free from all trace of acidity. They are then transferred to a narrow vessel, and kept melted therein until any contained water has completely settled out. 0·5 gramme of these acids is then weighed out and treated by the process already given under the analysis of fats (page 199). The "bromine substitution figure" for the fatty acids found in commercial soaps has been proved by the author to be practically nil, while that of resin, as usually employed in soap manufacture, is 105. Therefore every 1·05 of "bromine substitution figure" found will represent 1 per cent. of resin in the fatty acids, and this result multiplied by the percentage of fatty acids already found in the soap and divided by 100 will give the percentage of resin in the sample.

XIV. VALUATION OF DIGESTIVE FERMENTS.

(*a*) **Valuation of Pancreatin** (U.S.P. process). If there be added to 100 c.c. of tepid water contained in a flask 0·28 gramme of pancreatin and 1·5 gramme of sodium bicarbonate, and afterwards 400 c.c. of fresh cow's milk previously heated to 38° C., and the whole maintained at this temperature for half an hour, the milk should be so completely peptonised as to cease to be coagulable by the addition of nitric acid.

(*b*) **Valuation of Pepsin** (U.S.P. process). Prepare, first, the following three solutions:--

A. To 294 c.c. of water add 6 c.c. of diluted hydrochloric acid.

B. In 100 c.c. of solution *A* dissolve 0·067 gramme of the pepsin to be tested.

C. To 95 c.c. of solution *A*, brought to a temperature of 40° C. (104° F.), add 5 c.c. of solution *B*.

The resulting 100 c.c. of liquid will contain 2 c.c. of diluted hydrochloric acid, 0·00335 gramme of the pepsin to be tested, and 98 c.c. of water.

Immerse and keep a fresh hen's egg during fifteen minutes in boiling water; then remove it and place it into cold water. When it is cold, separate the white, coagulated albumin, and rub it through a clean sieve having 30 meshes to the linear inch. Reject the first portion passing through the sieve. Weigh off 10 grammes of the second, cleaner portion, place it in a flask of the capacity of about 200 c.c., then add one half of solution *C*, and shake well, so as to distribute the coherent albumin evenly throughout the liquid. Then add the second half of solution *C*, and shake again, guarding against foam. Place the flask in a water oven or thermostat, kept at a temperature of 38° to 40° C. (100·4° to 104° F.), for six hours, and shake it gently every fifteen minutes. At the expiration of this time the albumin should have disappeared, leaving at most only a few thin, insoluble flakes. (Trustworthy results, particularly in comparative trials, will be obtained only if the temperature be strictly maintained between the prescribed limits, and if the contents of the flasks be agitated uniformly, and in equal intervals of time.)

The relative proteolytic power of pepsin stronger or weaker than that described above may be determined by ascertaining, through repeated trials, how much of solution *B*, made up to 100 c.c. with solution *A*, will be required exactly to dissolve 10 grammes of coagulated and disintegrated albumin under the conditions given above.

Saccharated pepsin, when tested by this process, with the modification that 0·67 gramme of it is to be taken in preparing solution *B*, should digest 300 times its own weight of freshly coagulated and disintegrated egg albumin.

XV. ESTIMATION OF HYDROUS CHLORAL.

100 grains, dissolved in one fluid ounce of water and distilled with 30 grains of slaked lime, should yield 70 grains of chloroform.

In working with metrical weights we weigh out 5 grammes of the sample, place it in a small flask having a side tube attached for distillation (Erlenmeyer's), and add 25 c.c. of water, and 1·5 gramme of calcium hydrate. Cork the tube, and attach it to a short condenser, having a 10 c.c. graduated measure (showing $\frac{1}{10}$ c.c.) at the other end. Apply the heat of a water bath, and distil until all the chloroform has passed over, and collected in the measure beneath a slight layer of water. At the end of the operation read off the volume of the lower (chloroformic) layer, which should not be less than 2·34 c.c. To obtain the actual weight of the chloroform multiply its volume (in c.c.) by 1·49.

XVI. VALUATION OF MANNA.

Put 5 grammes of the manna into a flask with 80 c.c. of rectified spirit, and boil under an upright condenser for some time, till nothing more dissolves. Pour off rapidly into a tared basin, taking care that none of the insoluble matter comes into the basin. Cover up with glass plate, and set aside to crystallise. Pour off the mother-liquor, and, having allowed the crystals to become air-dried, weigh and deduct the tare of the basin. The crystals so obtained must not weigh less than 3 grammes, but in good samples they should be nearly 4 grammes. If an upright condenser is not handy, mark the flask at 80 c.c.; then start with 90 c.c. spirit, boil down to the 80 mark, and pour off.

XVII. ESTIMATION OF PHENOL.

The method for the determination of phenol quantitatively in ordinary carbolic acid has been already given under Volumetric Analysis (page 123).

When dealing with the so-called "commercial liquid carbolic acid" (which is not phenol, but a mixture of cresol with some higher phenols, and a trace of naphthalin), and of the disinfecting powders made therefrom, this process is practically useless. An approximation to the truth may be made by using Calvert's No. 5 acid as a standard to set the "hypo," but it is better to employ the process devised by the author, and given in full in "The Analyst," vol. xii., page 191, and vol. xv., page 63, to which reference is hereby made.

The amount of water contained in a solution of carbolic acid may be determined by agitating the solution, in a graduated cylinder, with an equal volume of chloroform. After standing, the upper layer consists of the water contained in the mixture. U.S.P.

XVIII. ESTIMATION OF GLYCERINE.

This process depends on (1) obtaining the glycerine free from other oxidisable bodies, such as alcohol, sugars, etc. (2) oxidising it with potassium bichromate in the presence of sulphuric acid to carbon dioxide and water by the following equation:—

$$3C_3H_5(OH)_3 + 7K_2Cr_2O_7 + 28H_2SO_4 = 7Cr_2(SO_4)_3 + 7K_2SO_4 + 9CO_2 + 40H_2O;$$

and (3) estimating the amount of CO_2 evolved.

The relation between carbon dioxide and glycerine is that 396 parts by weight of CO_2 represent 276 parts of glycerine, or, in other words, the weight in grammes of CO_2 found multiplied by ·69697 gives the amount of glycerine in the quantity weighed out for analysis. The process is conducted in an ordinary apparatus for the estimation of carbon dioxide like that figured on page 156, fig. 36. The fluid containing the glycerine is first tested for the presence of sugars, both cane and glucose, and if they are absent a measured quantity (say 100 c.c.) is evaporated on the water bath with 3 c.c. of milk of lime and 2 grammes of pure sand, till a fairly detachable residue is obtained. This is then scraped from the basin and extracted in the "Soxhlet" with absolute alcohol. The alcohol is distilled off in a weighed flask, and the weight of the residue taken. The residue is then dissolved in a little distilled water, and such an aliquot part taken for analysis as shall not contain more than ·5 gramme of glycerine. This is introduced into the apparatus with 4 grammes of potassium bichromate in saturated solution, and into the acid reservoir are placed 10 c.c. of strong sulphuric acid, the absorbing tube being also charged with the same acid. The apparatus is weighed, and then the acid in the reservoir is allowed to mix with the glycerine and bichromate. Action sets in, and after standing for three hours in a warm place, the whole is heated to gentle ebullition, cooled, and weighed. The loss of weight equals the CO_2 evolved, and this is then calculated to glycerine as above, and lastly corrected from the aliquot part to the whole. In the presence of sugar the liquid must first be inverted by boiling with dilute hydrochloric acid (if cane sugar be present), and then evaporated with an excess of barium hydrate instead of lime. This will either decompose the sugars, or render them insoluble in the alcohol subsequently applied.

XIX. ANALYSIS OF ESSENTIAL OILS.

1. **Physical Constants.** The specific gravity and the specific rotation in the polariscope, using a tube 100 m.m. long at a temperature of 15° C., are of importance, although variable within narrow limits. The following are the average results with a few of the chief oils :—

No.		Sp. Gr.	Optical rotation.
1	Oleum Anethi	·918	+ 63·5.
2	,, Anisi	·985 (at 20° C.)	− ·80 to − 1·20.
3	,, Aurantii	·851	+ 95.
4	,, Bergamottæ	·886	+ 5 to + 15 (average 10·00).
5	,, Cajuputi	·930	very slight in either direction.
6	,, Carui	·920	+ 75 to + 85 (average 80·
7	,, Caryophylli	1·055	inactive or very slightly −.
8	,, Cassiæ	1·060	inactive.
9	,, Cinnamonii	1·040	,,
10	,, Cubebæ	·925	− 40.
11	,, Eucalypti	·920	+ 2·5.
12	,, Juniperi	·850 (increasing by age)	− 7 (disappearing by age)
13	,, Lavandulæ	·882 ,, ,, ,,	− 7 to − 10 (decreasing by age).
14	,, Limonis	·859	+ 60.
15	,, Menthæ pip.	·900 to ·920	− 20 (English) − 12 (American)
16	,, ,, vir.	·930	− 49
17	,, Myristicæ	·910	+ 16.
18	,, Pimentæ	1·040	− 4.
19	,, Pini Sylvestris	·880	+ 10.
20	,, Rosmarini	·900	+ 5.
21	,, Santali	·970	− 20.
22	,, Sinapis	1·020	inactive.

The boiling point is scarcely ever constant, as these oils are always mixtures, and therefore require fractional distillation in a proper dephlegmator. The results so much depend on the apparatus employed, that it is hopeless to get any agreement in this respect between different operations, until an official method is definitely laid down. If, however, 50 c.c. of the oil be distilled from a long-necked Erlenmeyer's flask of 100 c.c. capacity, with a thermometer in the neck, and placed on a piece of wire gauze, to which heat is directly applied by a Bunsen burner, fairly concordant estimations may be made on successive quantities.

The following table shows the boiling points of the chief constituents of the common oils within a few degrees of which the chief fraction should be obtained. To save repetition, the numbers refer to the oils as arranged in the gravity and rotation table given above:

Constituents	Boiling points (C.).	Oils in which found
Anethol $C_6H_4.C_3H_5.OCH_3$	234	No. 2.
Cadinene $C_{15}H_{24}$	275	No. 12.
Carvol	224	Nos 1, 6
Cineol (Eucalyptol) $C_{10}H_{18}O$	176	Nos 5, 11
Cubebenes $C_{15}H_{24}$	260° to 280°	No. 10.
Eugenol $C_6H_3.OCH_3.OH.C_3H_5$	250	Nos 7, 18.
Limonene $C_{10}H_{16}$	176	Nos 1, 3, 6, 14
Menthol $C_{10}H_{19}OH$	212	No. 15.
Myristicol	270°	No 17
Pinene $C_{10}H_{16}$	155°	Nos 12, 17, 19, 20

2. **Chemical Analysis**. When the active constituents of essential oils are not simple mixtures of terpenes, they are usually capable of chemical determination. Many of the processes are, however, still in their infancy, and capable of great improvement. The active principles met with may be divided into six classes as follows: (*a*) Esters (compound ethers); (*b*) Phenols or phenolic ethers; (*c*) Aldehyds; (*d*) Ketones; (*e*) Alcohols; (*f*) Isothiocyanates. They may be respectively estimated as follows:

(*a*) *Estimation of Esters*. A weighed quantity of the oil (say 5 to 10 grammes) is placed in a strong glass flask of 100 c.c. capacity, capable of withstanding pressure, and to this is added 25 c.c. of a solution of 10 grammes KHO in 100 c.c. alcohol. The flask is closed by a cork, through which passes a / tube containing one inch of mercury, and placed on the water bath for two hours. At the end of that period it is removed from the bath, cooled, and its contents washed into a 250 c.c. flask, and made up to the mark with distilled water. This solution is then titrated with $\frac{N}{2}$ HCl, and the number of c.c. noted as *titration No.* 1. While the saponification is proceeding another 25 c.c. of the alcoholic potash is diluted to 250 c.c. with distilled water, and also titrated with $\frac{N}{2}$ HCl, and noted as *titration No.* 2. The volume of HCl used in titration No. 1 is deducted from that taken for titration No. 2, and the difference represents the alkali absorbed during the hydrolysis of the ester expressed in terms of $\frac{N}{2}$ KHO. The following is the equation for calculation of linalool acetate in oils of bergamot and lavender, and of the isomeric bornyl acetate in oil of pine:

$$\underset{\substack{196 \\ 98}}{CH_3CO.OC_{10}H_{17}} + \underset{\substack{56 \\ 28}}{KHO} = C_{10}H_{17}OH + CH_3COOK$$

Therefore each c.c. of $\frac{N}{2}$ KHO absorbed = ·098 grammes of the ester in the weight of oil started with.

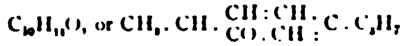
(*b*) *Estimation of Phenols and Phenolic Ethers*. Such bodies are met with in anethol $C_3H_5.C_6H_4.OCH_3$ (in oil of *anise*) and eugenol $C_6H_3.OCH_3.OH.C_3H_5$ (in oils of *clove*, *cinnamon*, and *pimento*). The former does not require chemical analysis, because pure anise oil melts at 18° to 20° C., and the melted liquid does not boil under 230° C.; but the latter may be estimated by mixing 5 grammes of the oil with

20 grammes of a 15 per cent. solution of NaHO, and then adding 6 grammes benzoyl chloride. On cooling crystalline benzoyl-eugenol ($C_6H_3 . OCH_3 . OC_6 . H_5CO . C_3H_5 = 268$) separates out. These crystals are washed by thrice melting them with 50 c.c. of hot water, stirring, and filtering off. The crystalline mass is then recrystallised from 25 c.c. of hot 90 per cent. alcohol, and the crystals, having been collected on a small tared filter, are washed with 90 per cent. alcohol till the whole filtrate measures exactly 25 c.c., then dried first by pressure between blotting paper, and finally in a weighing bottle at 100° C. The weight of the crystals + ·55 (allowance for solubility in 25 c.c. alcohol) $\times \frac{164}{268}$ = eugenol in the 5 grammes started with. A more rapid process is to warm a known volume of clove oil with 10 per cent. solution of potash, and then read off the volume of the uncombined oil in a graduated tube. The difference is the eugenol.

(*c*) *Estimation of Aldehyds.* Such bodies are met with as cinnamic aldehyd $C_6H_5 . C_2H_2 . CHO$ (in oils of *cinnamon* and *cassia*), benzoic aldehyd (in oil of *bitter almonds*), citral $C_{10}H_{16}O$ (in oil of *lemon*), etc., and to estimate them advantage is taken of the well-known reaction of aldehyds with sodium or potassium bisulphite, whereby a crystalline compound is produced which is soluble in water. Twenty grammes of the oil are shaken in a flask with 100 c.c. of a boiling 30 per cent. solution of sodium bisulphite, and then set aside for two hours. As much more water having been added and the whole warmed until the crystals dissolve, the contents of the flask are transferred to a separator, and the aqueous solution run off into another separator, where it is cooled and shaken up with 100 c.c. of ether. The aqueous layer having been removed, the ether is used to wash the contents of the first separator into a tared flask, from which the ether is distilled off, and the residual oil dried at 100° and weighed. This weight, *minus* the tare of the flask, deducted from the 20 grammes started with, and × 5, gives the aldehyd percentage. More roughly, this can be done by simply shaking up 10 c.c. of the oil in a suitable graduated measure (a burette answers well) with excess of hot saturated solution of sodium bisulphite, and then reading off the volume of the uncombined oil which floats, multiplying by 10, and deducting the answer from 100. This idea is taken advantage of qualitatively for the detection of imitation oil of bitter almonds (*oil of mirbane* or *nitrobenzol*) in the true oil by the U.S.P., which says :—

If 5 c.c. of the oil be vigorously shaken in a flask with 50 c.c. of a cold saturated solution of sodium bisulphite, and the mixture heated for a few minutes on a water bath, the odour of the oil should disappear, and a nearly clear solution be formed, without the separation of any oily drops on the surface of the liquid (absence of *most other volatile oils* and of *nitrobenzol*).

(*d*) *Estimation of Ketones.* Applicable to carvol—



$$C_{10}H_{14}O, \text{ or } CH_3 . CH . \begin{matrix} CH : CH . \\ CO . CH : \end{matrix} C . C_3H_7$$

(in oils of *carraway*, *dill*, and *green mint*). Five grammes of the oil are dissolved in 5 c.c. of alcohol, and sulphuretted hydrogen is passed to saturation. The resulting crystalline mass is washed on to a filter by the aid of another 5 c.c. of alcohol saturated with H_2S. The filter and contents are submitted to pressure in blotting paper till all the liquid is pressed out. The crystals are then removed from the paper to a small separator, decomposed with potash, and the carvol transferred to a tared beaker (using absolute alcohol to remove the last traces), and dried at 100° C. till constant ; or, they are decomposed with potash in a graduated tube, and the carvol which separates is measured. By this process the carvol is first precipitated as $(C_{10}H_{14}O)_2H_2S$,

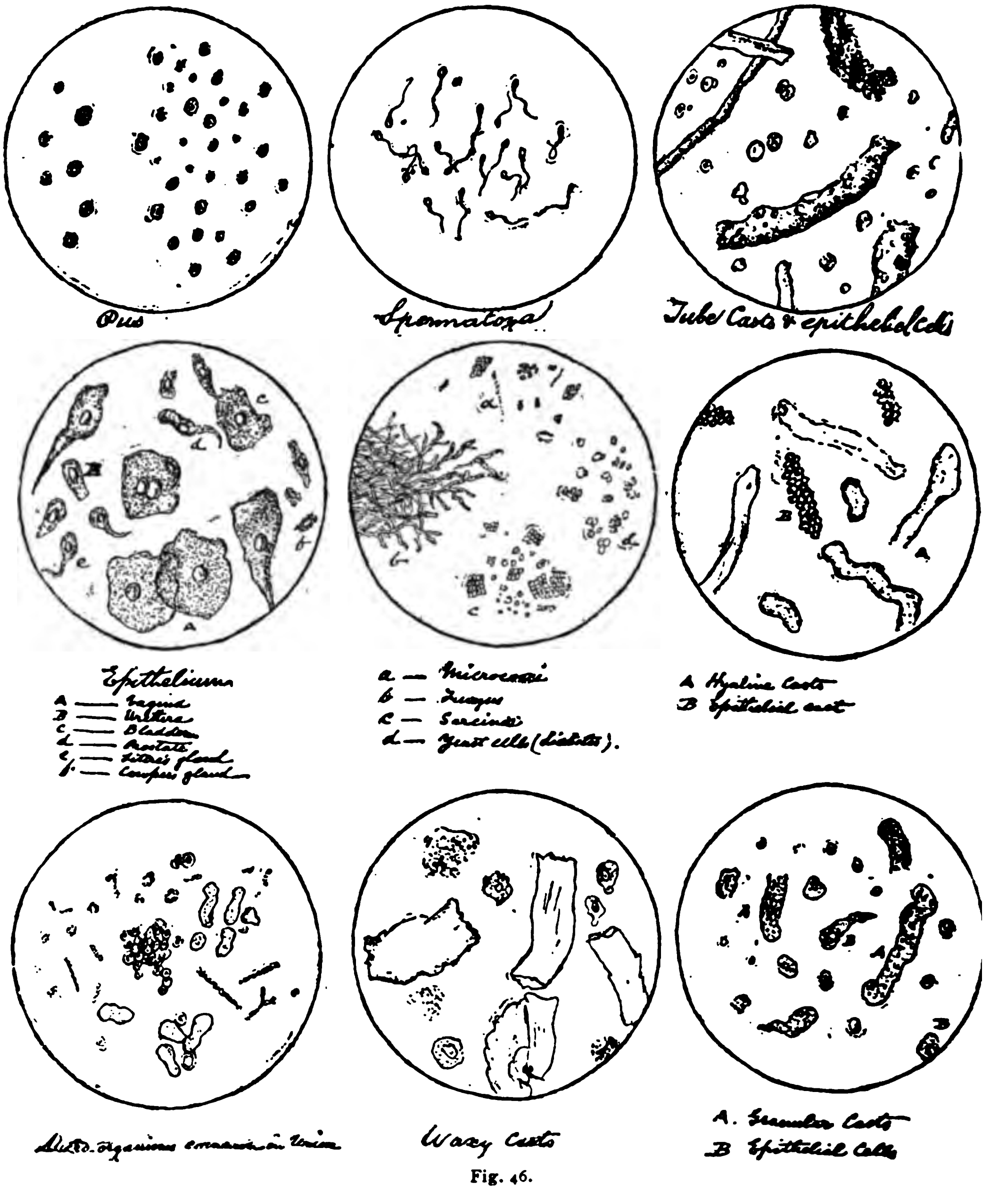
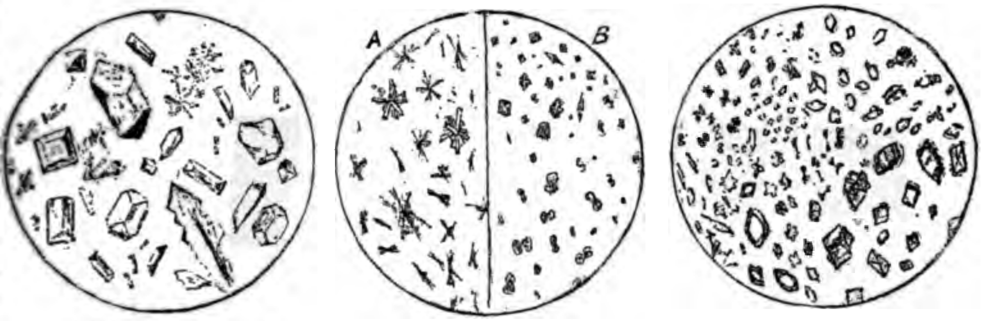


Fig. 46.

and then again liberated for weighing. Carvol may also be precipitated by phenyl-hydrazine as $C_{10}H_{14}.N.NH.C_6H_5$, and this body purified and weighed, but the results are not so good, owing to loss in purifying and drying.

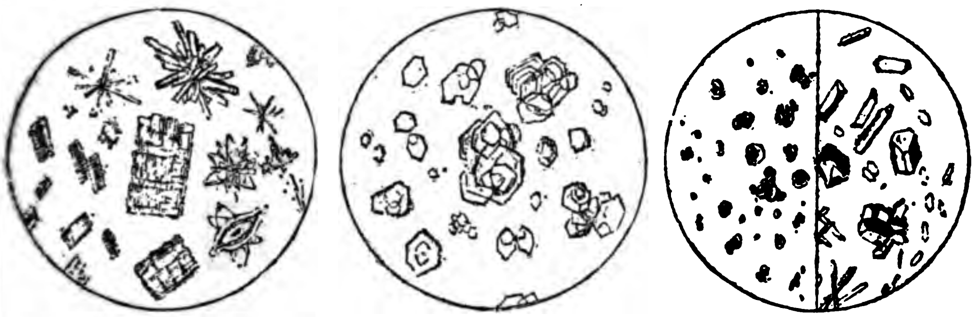
(*e*) *Estimation of Alcoholic Bodies.* Applicable to menthol $C_{10}H_{19}OH$ (in oil of *peppermint*) and borneol $C_{10}H_{17}OH$ (in oil of *rosemary*). The alcohol is first converted into its acetic ester by boiling 10 grammes of the oil under an upright condenser for two hours, with 10 grammes of anhydrous acetic



Triple Phosphate

A – Urates
B – Calcium oxalate

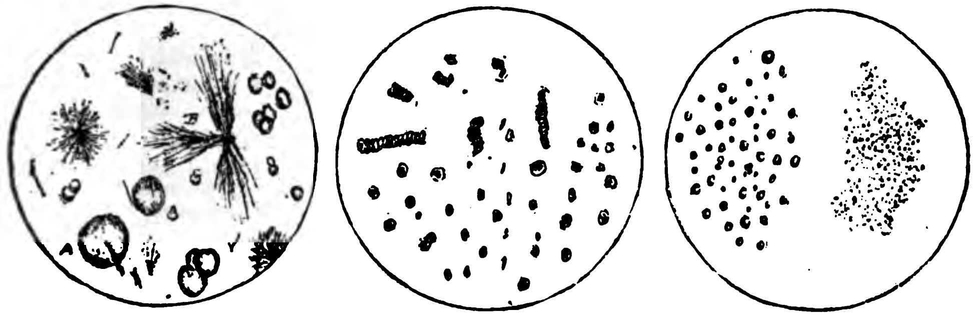
Uric Acid



Uric Acid

Cystin

A. Calcium carbonate
B. Hippuric acid



A – Leucin
B – Tyrosin

Blood discs

Fat globules

Fig. 47.

acid and 1 gramme of fused sodium acetate, when the following reaction takes place:—

$$C_{10}H_{19}OH + (CH_3CO)_2O = C_{10}H_{19}OCH_3CO + CH_3COOH.$$

The whole is washed into a separator, and there shaken up with successive quantities of water, until the washings run free from acidity. The menthyl acetate (or bornyl acetate) is then dried over calcium chloride and treated by the process for esters [(*a*) page 206]. Each c.c. of the $\frac{N}{2}$ KHO absorbed corresponds to ·078 menthol or ·077 borneol in the weight of oil started with.

(*f*) *Estimation of Allylisothiocyanate* (in essential oil of *mustard*). This is best done by placing 5 grammes of the oil in a tared platinum dish, dissolving in 5 c.c. of alcohol, and then adding an equal volume of solution of ammonia. By such means we obtain allylthiourea thus :—

$$\underbrace{C_3H_5NCS}_{99} + NH_3 = \underbrace{CS{<}\begin{matrix}NH\,.\,C_3H_5\\NH_2\end{matrix}}_{116}$$

The contents of the dish are then slowly evaporated and finally dried at 70° C., till constant and weighed. This weight − dish tare × $\frac{99}{116}$ = allylisothiocyanate in the oil started with.

DIVISION II. ANALYSIS OF URINE.

A sample of urine taken for analysis should be that first passed by the patient in the morning, or, better, a portion taken from the total twenty-four hours' urine.

The following are the chief points on which information is usually required by the physician who submits urine for examination to an analyst :—

1. Take the specific gravity, which should range from 1·015 to 1·025 at 60° F. For every 1° F. above 60° add ·0001 to the observed specific gravity. By multiplying the last two decimals of specific gravity by 2·33 we have the grammes per litre of total solid matter. Make a note also of the daily quantity, which should be 1200 to 1500 c.c. (40—50 fl. oz.). On standing some time urine undergoes ammoniac fermentation, and becomes alkaline in reaction.

Note. In diabetes the gravity is too high, sometimes reaching 1·060, while in albuminuria it is abnormally low, even occasionally falling to 1·005.

2. Examine the reaction, which should be very faintly acid.

3. Set a portion to settle in a long glass, and examine the deposit under the microscope for calcium oxalate or phosphate, uric acid or urates, pus, casts or kidney tubes, etc., etc. (See pages 208 and 209, and fig. 50, p. 213.)

Note.—The nature of the deposit may also be confirmed chemically as follows :—

(*a*) Warm the urine containing the sediment, when, if the latter should dissolve, it consists entirely of urates. In this case let it once more crystallise out, and examine it by the ordinary course for Ca, Na, and NH_4, to ascertain the bases.

(*b*) If the deposit be not dissolved by heating, let it settle, wash once by decantation with *cold* water, and warm with acetic acid. Phosphates will dissolve, and may be reprecipitated from the solution by excess of NH_4HO filtered out, well washed with boiling H_2O, dissolved in $HC_2H_3O_2$, and examined for Ca or Mg by the usual course for these metals in presence of PO_4.

(*c*) If the deposit be insoluble in acetic acid, warm it with HCl. Any soluble portion is calcium oxalate, which may be precipitated by NH_4HO.

(*d*) If the deposit be insoluble in HCl, it is probably uric acid. In this case apply the *murexid* test as follows: Place it in a small white dish, remove moisture by means of a piece of bibulous paper, add a drop or two of strong HNO_3, and evaporate to dryness at a gentle heat. When cold add a drop of NH_4HO, which will produce a purple colour, deepened to violet by a drop of KHO.

4. Test for albumin, as follows :—

(*a*) *Boiling test.* Filter the urine, place 10 c.c. in a narrow test tube, and add one drop of acetic or nitric acid. Heat the tube over a small flame in such a way that the *upper* portion of the liquid only shall be heated. Coagulation will take place, and the presence of albumin will be evident from the formation of a turbidity ranging from a faint cloud to a dense coagulum, but always strongly contrasted with the clear liquid beneath, which was not heated. Mucin also precipitates with this test.

(*b*) *Nitric test.* To five volumes of cold *saturated* solution of magnesium sulphate add one volume of nitric acid (sp. gr. 1·42), and preserve this reagent for use. Pour some perfectly clear filtered urine into a tube, and carefully add an equal volume of the reagent, delivered gently from a pipette, so that the liquids shall not mix. An opalescent zone will form at the point of contact either immediately or within twenty minutes, according to the quantity of albumin present. This zone should not dissolve on gently warming, but should be a distinct ring at the bottom of the urine, and not a general haze near the top, which latter indicates *mucin.* If the zone of contact has a pink colour, *indican* or other colouring matter is excessive. Indican may be further confirmed by mixing equal volumes of urine, strong HCl, and chlorine water, which produces a violet colour, and may be estimated by colour titration with chloroformic solution of indigo of known strength.

(*c*) *Picric acid test.* Dissolve 7·5 grammes of pure crystallised trinitro-phenol (picric acid) in 500 c.c. of water, let it stand for some days to perfectly clarify, pour off, and preserve the reagent for use. Mix some of the filtered urine in a tube with an equal volume of this reagent, look for any cloud or precipitate, and then heat to boiling. The true albumin cloud will remain permanent, while that due to peptones or alkaloids accidentally present will be dissolved. Picric acid does not precipitate mucin, and is therefore a valuable confirmatory test.

(*d*) *Bödeker's method.* Take a drachm of the urine, acidulate it with acetic acid, and add some potassium ferrocyanide drop by drop till a clear excess has been added. If during the addition a precipitate forms, albumin is to be suspected. Mere traces require some time to cause the cloud.

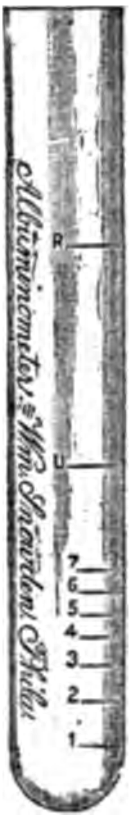


Fig. 48.

(*e*) *To estimate the albumin.* This may be done empirically by means of an *albuminometer* (fig. 48). Fill to U with the urine and R with the precipitant (picric acid 10 grammes, citric acid 20 grammes, and water to make 1000 c.c.). Mix by inverting the tube several times, not by agitation, and set aside for 24 hours. The height of the precipitate, as indicated by the graduations, represents the grains of albumin per thousand c.c. of urine. Be careful to read the height of the precipitate from the middle of the albuminous surface. If the urine is alkaline, make it acid with acetic acid. In the absence of such a convenient appliance we may take a weighed quantity of the urine, and allow it to drop into boiling water acidulated with acetic acid. Collect the precipitate on a tared filter, wash with boiling water, dry at 100 C., weigh, and deduct the weight of the filter, when the balance = albumin in the weight of urine operated upon.

5. Test for grape sugar, as follows:-

(a) *Moore's test.* Acidulate with acetic acid, boil, and filter out any albumin if necessary. Then mix the filtrate with equal parts of *liquor potassæ* and heat to boiling, when ordinary urine will turn brownish red, but saccharine urine will become dark brown or black.

(b) *Boettger's test* (modified by Nylander). Dissolve 2·5 grammes of *pure* bismuth oxynitrate (free especially from silver) and 4 grammes of Rochelle salt in 100 grammes of 8 per cent. solution of sodium hydrate, and preserve for use. To use this reagent 1 c.c. of urine is added to 10 c.c., and the whole boiled gently for some time, when if even only traces of sugar be present the mixture becomes black.

(c) *Fehling's test.* Render the urine alkaline with potassium hydrate, and filter to remove any phosphates, etc., which may precipitate. Boil the filtrate with Fehling's solution of copper (see page 130), and if a precipitate should form sugar is present.

(d) *To estimate the sugar.* This is best done by taking 10 grammes of the urine and diluting it with water to 100 c.c. Place this solution in a burette, and run it gradually into 10 c.c. of Pavy's or Fehling's solution, kept boiling in a flask as directed under the Volumetric Analysis of Sugar, page 130. The number of c.c. of urine used will contain ·005 gramme of grape sugar if Pavy's solution, or ·05 gramme if Fehling's, was used, and then $\frac{100 \times {\cdot}005}{\text{c.c. used}}$ (Pavy), or $\frac{100 \times {\cdot}05}{\text{c.c. used}}$ (Fehling) = sugar in the 10 grammes of urine taken.

(e) *Estimation of sugar by fermentation.* Take 1 gramme of commercial compressed yeast: shake thoroughly in the graduated test tube with 10 c.c. of the urine to be examined. Then pour the mixture into the bulb of the saccharometer (shown in fig. 49, page 213). By inclining the apparatus the mixture will easily flow into the cylinder, thereby forcing out the air. Owing to the atmospheric pressure the fluid does not flow back, but remains there. The apparatus is to be left undisturbed for 20 to 24 hours in a room of ordinary temperature. If the urine contains sugar, alcoholic fermentation begins in about 20 to 30 minutes. The evolved carbonic acid gas gathers at the top of the cylinder, forcing the fluid back into the bulb. On the following day the upper part of the cylinder is filled with carbonic acid gas. The changed level of the fluid in the cylinder shows that the reaction has taken place, and indicates by the numbers—to which it corresponds the approximate quantity of sugar present. If the urine contains more than 1 per cent. of sugar, then it must be diluted with water before being tested Diabetic urines of straw colour and a specific gravity of 1018 1022 may be diluted twice; of 1022—1028, five times. 1028—1038, ten times. The original (not diluted) urine contains, in proportion to the dilution, two, five, or ten times more sugar than the diluted urine

6. Test for bile, as follows:—

(*a*) *Oliver's test.* Dissolve 2 grammes of flesh peptone, ·25 gramme of salicylic acid, and 2 c.c. of 33 per cent. acetic acid in enough water to yield 200 c.c. of product. The solution should be rendered perfectly brilliant by passing it through frozen filtering paper. The urine, which should be very clear, is diluted to a specific gravity of 1·008. One cubic centimetre of this is added to 3 c.c. of Oliver's reagent. An opalescence at once appears, which will be found to be more or less distinct according to the quantity of bile salts present. Keller's contact method can be advantageously employed for applying the test.

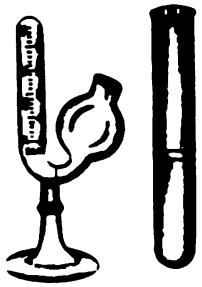


Fig. 49.

(*b*) *Gmelin's test for bile pigments.* Place a drachm of nitric acid in a test tube, and cautiously pour upon it an equal volume of the urine. In the presence of bile a play of colours from green to violet, blue, and red will be observed where the liquids touch.

(*c*) *Pettenkofer's test for biliary acids.* Mix equal parts of urine and sulphuric acid, add one drop of saturated syrup, and apply a gentle heat. If biliary acids be present, the colour will change from cherry-red to deep purple.

Note.—Bilious urine is usually of a brownish-green colour.

7. Test for urea, as follows:—

(*a*) Separate any albumin (as directed in Moore's test) if necessary, and evaporate an ounce of the urine to a syrupy consistence on the water bath. When cold add nitric acid, drop by drop, till crystals of nitrate of urea cease to deposit.

(*b*) *Estimation of urea.* This is performed by the hypobromite process already given at page 135. Normal urine contains 2 to 3 per cent.

8. Test for uric acid by mixing one ounce of the urine with one drachm of hydrochloric acid in a beaker, and set aside for some hours. The uric acid will be deposited in reddish-brown crystals, which may, if desired, be weighed and proved by the *murexid* test. Normal urine contains 3 to 7 parts per thousand.

A volumetric method is also used which is based on the known fact that argentic urate is insoluble in ammonia, but dissolves in nitric acid. The solutions required are:—1. "$\frac{1}{100}$ ammonium thiocyanate"; dissolve about 8 grammes of ammonium thiocyanate in a litre of water, and check with $\frac{1}{10}$ argentic nitrate solution; dilute it for use with nine volumes of water. 2. Dissolve 5 grammes of argentic nitrate in 100 c.c. of distilled water, and add ammonia until the solution becomes clear. 3. Dilute 70 per cent. nitric acid with two volumes of distilled water, boil, to destroy the lower oxides of nitrogen, and preserve from the action of light. 4. A saturated

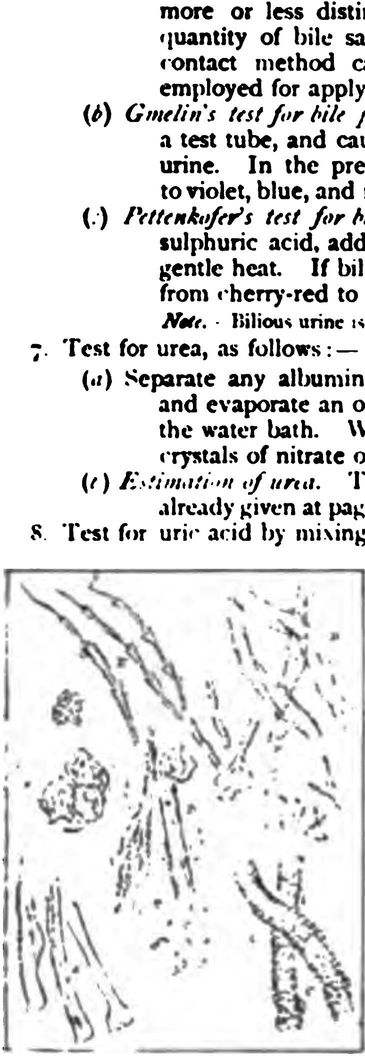


Fig. 50.—Extraneous Matters often seen in Urine. A, silk; B, cotton; C, wool; D, linen; E, feather; F, mycelium; G, cork.

solution of ferric alum. 5. Strong solution of ammonia. The following is a description of the process:—Place 25 c.c. of urine in a beaker with 1 gramme of sodium bicarbonate. Add 2 or 3 c.c. of strong ammonia, and then 1 or 2 c.c. (or an excess) of the ammoniated silver solution. A special procedure is necessary in order to collect the precipitate, as follows:—Fill a glass funnel to about one third with broken glass, and cover this with a bed of good asbestos to about a quarter of an inch deep. This is best done by shaking the latter in a flask with water until the fibres are thoroughly separated, and then pouring the emulsion so prepared in separate portions on to the broken glass. On account of the nature of the precipitate and of the filter, it is necessary to use a Bunsen water pump in order to suck the liquid through. Having thus collected the precipitate, wash it with distilled water until the filtrate ceases to become opalescent with a solution of NaCl. Now dissolve the precipitate by washing it through the filter into a beaker, with a few cubic centimetres of the special nitric acid. Estimate the silver by Volhard's method thus:—Add to the liquid in the beaker a few drops of the ferric alum solution to act as an indicator, and from a burette carefully drop in $\frac{N}{100}$ ammonium thiocyanate solution until a permanent red colour appears. The number of c.c. used, multiplied by 0·00168, gives the amount of uric acid in the 25 c.c. of urine. One milligramme may be added to this amount as an allowance for average loss, and the whole multiplied by 4 gives the percentage of uric acid in the urine. The sodium bicarbonate is added in the early part of the process, to prevent decomposition of the argentic urate, which would otherwise occur. This method has, however, been lately stated to be unreliable

9. Test for phosphates, as follows:

(*a*) Add to one ounce of the urine a slight excess of ammonium hydrate, and boil. $Ca_3(PO_4)_2$ and $MgNH_4PO_4$ will both be precipitated, and the precipitate, if more than a distinct cloud, should be filtered out, dissolved in HCl, and analysed by the ordinary process already given for phosphates.

(*b*) After filtering out the earthy phosphates as above, alkaline phosphates may be tested for by adding *magnesia mixture* to the filtrate, and getting the usual precipitate of $MgNH_4PO_4$ after standing some hours in a cold place.

(*c*) *Estimation of phosphates.* This is done by the volumetric process with uranic nitrate, already described at page 131. Normal urine contains 2 to 3 parts P_2O_5 per thousand

10. Test for sulphates, as follows:—

Acidulate a little of the urine with HCl, warm, and add excess of $BaCl_2$. If the precipitate appear too copious, estimate as usual, using 50 c.c. urine (see page 132). Normal urine contains 1·5 to 3 parts SO_3 per thousand.

11. Test for chlorides, as follows:

Acidulate a little of the urine with HNO_3, and add excess of argentic nitrate. If the precipitate thus produced looks very large, a weighed quantity of the urine should be taken, and the chlorides estimated by Volhard's method (see page 118). Normal urine contains 5 to 10 parts sodium chloride per thousand.

12. *Blood* is best seen under the microscope, but urine containing it has always a very characteristic smoky appearance. A test for blood is to add tincture of guaiacum and ethereal solution of hydrogen peroxide, which produce a sapphire blue; but such colour of itself should not be taken as positive proof without the blood discs beings also visible under the microscope.

DIVISION III. ANALYSIS OF URINARY CALCULI.

The following table will show at a glance the compositions and methods of proving the various calculi.

1. Calculi, fragments of which, heated to redness on platinum, entirely burn away.

NAME.	PHYSICAL CHARACTERS.	CHEMICAL CHARACTERS.
Uric acid, $C_5N_4H_4O_3$.	Brownish-red; smooth or tuberculated; concentric laminæ (common).	Insoluble in water; soluble in KHO by heat, but evolves no NH_3; dissolves with effervescence in HNO_3, and the residue on evaporating the solution is red and gives the *murexid* test.
Ammonium urate.	Clay-coloured; usually smooth, and rarely with fine concentric laminæ (uncommon).	Soluble in hot water; soluble in heated KHO, evolving NH_3. Behaves with HNO_3 like uric acid.
Cystine, $C_6H_{12}N_2S_2O_4$.	Brownish-yellow, semi-transparent and crystalline (very uncommon).	Insoluble in H_2O, alcohol, and ether. Soluble in NH_4HO, and depositing, when allowed to evaporate spontaneously, hexagonal plates. When heated, gives off odour of CS_2.
Xanthin, $C_5H_4N_4O_2$.	Pale polished brown surface (very uncommon).	Soluble in KHO; soluble in HNO_3 *without effervescence*, and the solution leaves on evaporation a deep yellow residue.

2. Calculi, fragments of which, heated to redness on platinum, do not burn away.

NAME.	PHYSICAL CHARACTERS.	CHEMICAL CHARACTERS.
Calcium oxalate, *mulberry calculus*, CaC_2O_4.	Deep brown, hard, and rough; thick layers (common).	Insoluble in acetic acid, but soluble, without effervescence, in HCl; heated to redness, it is converted into $CaCO_3$, which dissolves with effervescence in acetic acid, and the solution gives a white precipitate with $(NH_4)_2C_2O_4$. Heated strongly before the blow-pipe, CaO remains, which, when moistened, is alkaline to test-paper.
Tricalcium phosphate, *bone earth calculus*, $Ca_3(PO_4)_2$.	Pale brown, with regular laminæ (uncommon).	Infusible before the blow-pipe, and residue, when moistened, is not alkaline. Soluble in HCl, and the solution gives a *gelatinous* precipitate with excess of NH_4HO.
Magnesium ammonium phosphate, *triple phosphate calculus*, $MgNH_4PO_4$.	White, brittle, crystalline, with an uneven and not usually laminated surface (uncommon).	Fusible with difficulty before the blow-pipe, evolving NH_3, and residue not alkaline. Soluble in HCl, and solution gives white *crystalline* precipitate with NH_4HO.
Mixed phosphates of Ca, Mg, and NH_4, *fusible calculus*	White, and rarely laminated.	Readily fusible before the blow-pipe. Soluble in acetic acid, and solution gives a white precipitate with $(NH_4)_2C_2O_4$, and the filtrate from that precipitate gives a white precipitate with excess of NH_4HO.

CHAPTER XII.

THE TAKING OF MELTING, SOLIDIFYING, AND BOILING POINTS, POLARISATION ANALYSIS, SPECTRUM ANALYSIS, AND THE ANALYSIS OF GASES.

DIVISION I. THE TAKING OF MELTING, SOLIDIFYING, AND BOILING POINTS.

(1) **Melting Points.** Many methods have been from time to time proposed, but the following will be found to be sufficiently good for all ordinary purposes, and is, moreover, the method officially adopted in the Pharmacopœia.

A piece of narrow glass tube is softened in the gas flame and drawn out, so as to give it a long thin end with a capillary bore. The fat or wax is melted, and a little of it is sucked up into this capillary tube and allowed to solidify therein. The tube is then tied to a delicate thermometer, so that its capillary end (having the semi-opaque column of solidified fat inside) just rests against the bulb of the thermometer. Both are now supported perpendicularly in a beaker of water, and heat is gently applied to the same. The rise of the thermometer and the appearance of the tube of fat being both observed, the height of the former, at the moment when the column of fat becomes transparent, is noted as the melting point required. It is always useful to repeat the process three times and to take the average as the true melting point.

(2) **Solidifying Points.** It frequently happens, especially in solid fats, that this is a more constant factor than the melting point. We heat the substance to a temperature of about ten degrees above its melting point, and place it in a glass cylinder surrounded by cotton-wool. We then stir slowly with a delicate thermometer, and, as the liquid cools, the temperature regularly falls, until a moment arrives when, after a slight pause, the thermometer shows a sudden rise of a fraction of a degree. This is then the solidifying point of the fat.

(3) **Boiling Points.** Procure a test tube fitted with a cork through which is passed a delicate thermometer, and also a short tube bent twice at a right angle (thus ⊓) to allow of the escape of vapours. Introduce about 2 c.c. of the liquid, put in the cork and arrange the thermometer so that its bulb is just above the surface of the liquid, but not touching it. Now apply a suitable heat, when the mercury in the thermometer will rise until the liquid boils, and will then remain stationary until all has evaporated. The point to which the mercury thus rises is the boiling point of the liquid. With certain substances (such as melted hydrous chloral) which do not boil without "bumping," it is necessary to introduce a few fragments of broken glass or recently ignited clay tobacco pipe. All boiling points are supposed to be taken under a normal barometric pressure (760 mm., or 29.9 inches), therefore we must

always read the pressure for the day, and either add to or deduct from the observed boiling point 0·1° C. for every 2·7 mm. of barometric variation.

DIVISION II. ANALYSIS BY CIRCULAR POLARISATION.
THE SACCHAROMETER.

Crystals which do not belong to the regular system (notably calc-spar) possess the power of *double* refraction. That is to say, when a ray of light falls upon them, it is divided into two rays, one of which follows the ordinary rule of refraction, while the other takes a totally different course; and the two rays are called respectively the "**ordinary**" and the "**extraordinary**" ray. The most convenient polarising medium is what is called a "**Nicol's prism.**" It is composed of a crystal of calc-spar cut into two portions in the direction of its axis, and the two parts thus obtained cemented together with Canada balsam. When a beam of light enters the prism, it is doubly refracted by the *first* portion of the crystal, and the **extraordinary** ray only passes through the **second** portion to the eye of the observer; while the **ordinary** ray is completely reflected away by the layer of Canada balsam, and so lost to view. When this extraordinary ray is examined, it is found to possess peculiar properties, such as showing colour in transparent bodies which are usually colourless. This is accounted for by believing that it has become **polarised**—*i.e.*, that all its vibrations have been reduced to the same plane. If the polarised light thus obtained be examined by means of another Nicol's prism, it will be found that, when the two prisms are placed with the principal sections parallel to each other, the ray will pass freely; but if the second prism, called the analyser, be then turned round, so that its chief section is at right angles to that of the first, the polarised ray will in turn be entirely reflected from the layer of balsam, and no light will now reach the observer's eye. This holds good so long as nothing intervenes between the two prisms; but it has been found that certain bodies, such as quartz, possess the power, when interposed between the prisms, of giving a colour instead of darkness, owing to their possessing the power of twisting the polarised ray from its original plane. Such substances are said to possess the power of **circular polarisation**, either in a "right-handed" or "left-handed" direction, according as it is necessary to turn the prism either to the right or left from its proper position, to once more produce complete passage of the colourless polarised ray. The direction of the rotation is indicated by the use of arrows, thus: ↶↷. Cane sugar, grape sugar, dextrin, maltose, creasote, camphor, turpentine (*American*), cinchonine, castor oil, croton oil, and lemon oil, rotate the plane of the polarised ray to the right; while fruit or (invert) sugar, quinine, cinchonidine, turpentine (*French*), and many essential oils, morphine, etc., have a left-handed rotation.

There are two varieties of quartz, known as right-handed and left-handed, one of which rotates the plane of polarisation to the right, and the other to the left. If a plate of quartz 1 millimetre thick be placed between the two "Nicol's," the ray of polarised light is rotated, and, instead of being colourless, is coloured, changing to all the colours of the spectrum as the analyser is turned, until it once more becomes colourless, and the amount that the analyser has to be turned (registered by a pointer on the degrees of the circle) is the index of rotary polarisation possessed by the quartz either in a right or left-handed direction. If the turning of the analyser be now continued, colour will again show itself, but this time it will be the colour *complementary* to that at first produced. Thus, if we start with a plate of quartz showing red between the uncrossed prisms, and rotate, we shall find that, when we have turned through an angle of 45°, we get no colour, but after that we begin to get the complementary colour green, which becomes most intense at the right angle of 90°, when the prisms are crossed. The polariscope as used for analysis is therefore essentially (*a*) a Nicol's prism acting as a polariser, (*b*) a plate of quartz usually divided down the centre, the one side being right-handed and the other left, (*c*) a tube to contain the solution, (*d*) another "Nicol" capable of being rotated, and having a pointer acting on degrees of the circle on a scale, (*e*) a telescope to focus the line between the two sides of the quartz. When the pointer is placed at *zero*, the tube filled with water, and the line focussed, no colour is seen on either side of it; but if a solution, say of sugar, be introduced, colour appears on one side of the line according to the nature of the sugar, and then the distance through which the pointer has to be moved round the graduated circle to get both sides of the quartz colourless is the degree of rotary polarisation. In practice, monochromatic light from a sodium flame is employed, which causes a dark shadow, instead of a colour, to appear when the instrument is used, so enabling colour-blind persons to employ it without difficulty. Another reason for the employment of a definite monochromatic light lies in the fact that the rotating power of bodies alters according to the ray of the spectrum used, being least for the red rays, and increasing till it reaches its highest point at the violet end of the spectrum. Optical determinations are made in a dark room, and the instrument is illuminated by a bead of fused sodium chloride held by a platinum support in a "Bunsen" flame. Light thus obtained corresponds to that emitted at the D line of the solar spectrum.

Since the deviation of the plane of polarisation either to the right or to the left of the zero point is directly proportional to the length of the column of liquid, it is important that the observations should be made with tubes of a definite length, such as 100, 50, or 25 mm. The selection of the length of the tube to be employed is, however, usually dependent upon the depth of colour of the liquid and the extent of its optical rotation. The rotatory power of an optically active, liquid substance, observed with sodium light, and referred to the ideal density 1, and in a tube having a length of 1 decimetre (100 mm.), is designated as its *specific rotatory power*. This is usually expressed by the term $[\alpha]_D$. Since, however, not only the density of an optically active liquid, but also its rotation, is influenced by the temperature, the specific rotation varies with the latter. In stating the specific rotation, it is therefore necessary to indicate at what temperature the rotation and the density of the liquid have been determined. But for the same temperature the specific rotation of a pure, optically active liquid is always a constant number. To use the instrument we make a solution of the body to be examined of a definite percentage strength by dissolving a certain number of grammes in 100 c.c. of a solvent. We then fill the tube, observe the degree of rotation produced, and from that we calculate the absolute angle of rotation for the sodium light (always expressed as $[\alpha]_D$) by the following formula and factors:—

I. For liquid substance $[\alpha]_D = \dfrac{100 \times a}{l \times d}$

II. For solutions of solids $\begin{cases} [\alpha]_D = \dfrac{10000 \times a}{l \times p \times d} \\ \text{or } [\alpha]_D = \dfrac{10000 \times a}{l \times c} \end{cases}$

a = the angle of rotation of the liquid or solution observed with sodium light.
l = the length of the tube in millimetres.
d = the density or specific gravity of the active liquid.
p = the amount of active substance in 100 parts by weight of the solution.
c = the number of grammes of active substance in 100 c.c. of the solution.

If the absolute angle thus found coincides with that obtained from the same substance in a state of purity, then the article under examination is pure; but if not, then a simple percentage calculation gives the impurity.

Thus the $[\alpha]_D$ of pure cane sugar = 66·5. A sample examined as above gave an $[\alpha]_D = 65{\cdot}5$

Then: $\frac{65{\cdot}5 \times 100}{66{\cdot}5}$ = per cent. of real sugar present in the sample.

DIVISION III. SPECTRUM ANALYSIS.

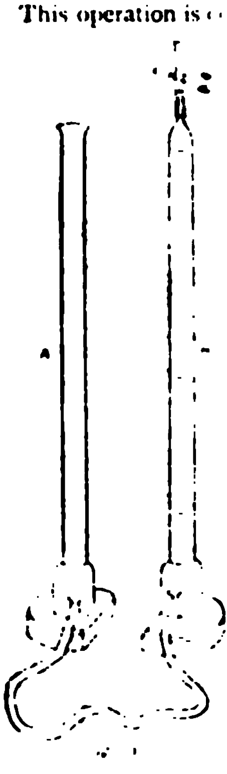
When a ray of sunlight is allowed to pass through a prism, it is deflected and *dispersed* into a number of rays differing in their degree of refrangibility. When these rays, as they pass from the prism, are caused to fall upon a white surface, they are observed to have a marked difference in colour. The image so produced is called a **spectrum**; and when sunlight is thus treated it is found to give a spectrum consisting of the following colours—viz., violet, indigo, blue, green, yellow, orange, and red. The violet end of the spectrum, owing to its greater refrangibility, is always the nearer to the base or broad end of the prism. By this means of separating the rays of light we are able to ascertain the peculiar properties of each of the colours which go to compose it, and we find that the chemical activity of light resides chiefly in the most highly refrangible rays just outside the violet end of the visible spectrum, which are called the actinic rays; while, on the other hand, the heat transmitted by the sun is most felt at the opposite or red end of the spectrum.

Further research has demonstrated that, if we substituted the light emitted from various bodies in a state of incandescence to the action of a prism, the image or spectrum produced varied in each case, and was, moreover, almost characteristic of the particular bodies employed. This discovery led to the invention of the spectroscope, which, in its simplest form, consists of a metallic diaphragm with a narrow slit, through which a ray of light from the burning body is allowed to pass and is condensed by a lens upon a prism of glass, or, better still, a triangular bottle of thin glass filled with disulphide of carbon. At the opposite side of the prism is a short telescope, so arranged that an observer, looking through it, sees the spectrum or image produced by the light after passing through the prism. This telescope works upon a graduated scale, by which its position for viewing any particular line observed can be noted.

When ordinary solar light is examined through the spectroscope, a number of dark lines are found crossing the image at certain fixed points. They are called "**Fraunhofer's lines**," and their position is characteristic of sunlight. It has been proved that such lines are only formed when the source of light contains volatile substances, as we find that the light emitted by a non-volatile heated body gives a continuous image, devoid of lines. If, for example, a platinum wire be heated to a high temperature in a Bunsen burner, and the light thus produced be examined, no lines will be visible; but if the wire be now tipped with a fragment of sodium chloride, and once more ignited, a bright line will suddenly appear in the yellow of the spectrum, and in so dazzling a manner as to render the whole of the rest of the image almost invisible. In carrying out this system of analysis, therefore, it is only necessary to procure a perfectly clean piece of platinum wire, with one end bent into the form of a loop, and place a Bunsen gas burner in such a position that the rays from anything heated in it will pass into the spectroscope. The wire is then to be moistened with a little hydrochloric acid, and, having been dipped in the substance to be examined, is to be held in the hottest portion of the Bunsen flame, and its spectrum simultaneously observed through the spectroscope, noting carefully the colour, number, and position on the scale, of the bright lines produced. When thus examined we find that potassium exhibits one bright line in the red, and one in the blue; lithium, one bright line in the yellow, and one more brilliant in the red; strontium, one blue, one orange, and six red lines; barium, a number of lines chiefly green and yellow; calcium, three distinct bright yellow lines, one within green, and some broad but indistinct ones in the orange and red; and lastly, sodium, the single bright yellow line already mentioned.

The student must commence with the examination of pure salts, carefully noting for reference the position of the index of the telescope on the scale where each characteristic line is found. When it is desired to examine any mixture, the telescope index is brought to the required position and the substance is examined; if the proper line is seen, then the element searched for is present; if not, it is absent. If we examine ordinary light which has been made to pass through solutions of various coloured bodies, we obtain dark bands analogous to the lines of Fraunhofer. These are called **absorption spectra**, and are very useful in the detection of soluble colouring-matters. A solution of blood, for example, shows characteristic bands in the green of the spectrum. All this is a matter of special study, and to go farther into it would be beyond the scope of this volume.

DIVISION IV. THE ANALYSIS OF GASES.



This operation is conducted by measuring a volume of the mixed gas under definite conditions of temperature and pressure, then exposing it to the action of some substance having the power of absorbing some one constituent of the mixture, and again measuring the gas left. By seeing that the inside of the measuring tube is always kept moist the question of tension of aqueous vapour is equalised all through the experiment, and as many absorbents as may be necessary are employed in turn. Many of the gas-measuring appliances are large, costly, and require to be kept in special rooms devoted to the purpose. Hempel has, however, devised a gas-measuring apparatus which is reasonable in price, and yet is capable of measuring gas volumes with very fair accuracy. It consists essentially of a vessel for measuring volumes of gas known as a **Gas Burette**—and a number of other vessels called **Gas Pipettes**—in which the necessary absorptions are carried out.

The **Gas Burette** (fig. 51) is an arrangement similar to the Nitrometer already fully described at page 133, and is composed of two tubes, A and B. The tube B is graduated in cubic centimetres, and has a capacity of 100 c.c. It is closed at by a piece of india-rubber tube and a pinch-cock, and at *d* is connected by a long flexible tube with A. To measure off a volume of gas insoluble in water, the two tubes are *completely* filled with water, c is closed and A is partially emptied. Connection is now made at c with the vessel containing the gas, c is opened, the gas flows into B and an equal volume of water runs into A (which is placed on a lower level if necessary), and after adjusting the level of the water in the two tubes the volume is read off.

Of the **Gas Pipettes** there are three forms. Fig. 52 is a *single pipette*, and has two bulbs, E and F, connected by a tube, *t*. The bulb E terminates in a capillary tube *k*, by which connection is made with the gas burette. In using the pipette E is completely filled with the reagent intended to act on the gas. The gas burette is closely connected with *k* by means of a small black rubber tube, and by raising A and opening C the gas is forced into E, part of the reagent into F. After the absorption—which may be quickened by shaking—is completed, the gas is again allowed to flow back into B, *c* is closed, the water levels are adjusted, and the volume is read off as before.

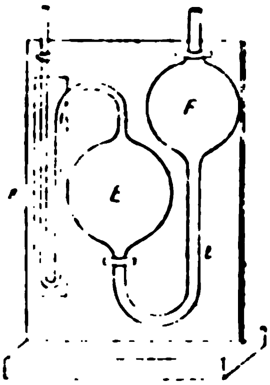


Fig. 52.

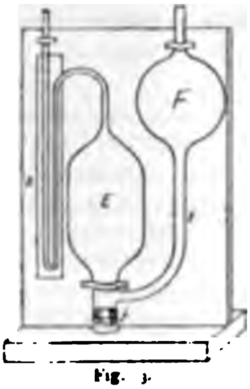


Fig. 53.

Fig. 53 is a modification with an opening at *f* closed by a cork. It is adapted for use with solid reagents, *e.g.*, moist phosphorus for the absorption of oxygen.

Fig. 54 is a *compound absorption pipette*, and is for use with solutions which require to be preserved from the action of the oxygen of the air, such as alkaline solution of potassium pyrogallate for absorbing oxygen, or ammoniacal cuprous chloride for absorbing CO. The bulb E is filled with the solution, the bulb G with distilled water. By means of the water in G the solution is exposed to the action of only a small quantity of air in F, which is quickly deprived of its oxygen, and thus the absorbing power of the solution remains unimpaired.

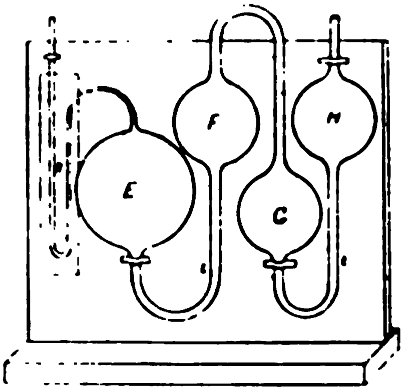


Fig. 54.

To perform an analysis 100 c.c. of gas are measured off in the burette, this volume being chosen so that the result of each absorption may represent, without calculation, the percentage of volume of the absorbed gas contained in the mixture. As many pipettes are prepared and furnished with the necessary reagents as there are constituents in the gas. The gas is then passed into each of these, allowed to remain a sufficient time for the absorption to take place, again collected in the burette, and the change of volume noted.

The chief absorbents employed in gas analysis are as follows, it being understood that it is necessary to employ them in such an order as shall be suitable to the particular mixture of gases under analysis :—

A. Strong solution of potassium hydrate absorbs CO_2.

B. 1 vol. of 25 per cent. solution of pyrogallic acid + 6 vols. 60 per cent. solution of KHO absorbs O_2 (after removal of any gas absorbed by KHO alone).

C. Moist phosphorus absorbs oxygen, but not CO_2.

D. Concentrated solution of cuprous chloride in dilute hydrochloric acid absorbs CO (after removal of CO and O_2 with alkaline pyrogallate).

E. Ammoniacal solution of cuprous chloride absorbs C_2H_2, after removal of CO, CO_2, and O.

F. Palladium black absorbs hydrogen, but not CH_4. The palladium black is contained in a U tube, one limb of which is connected to the burette, the other to a simple absorption pipette filled with water. The gas is passed backwards and forwards over the palladium several times, and complete absorption takes place.

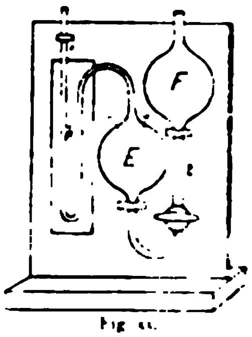


Fig. 55.

G. A solution of sulphuric anhydride in strong sulphuric acid, or solution of bromine, absorbs C_2H_4, and the other gaseous hydrocarbons of the series C_nH_{2n}, and of C_nH_{2n-2}.

H. The addition of an excess of pure oxygen, and absorption with alkaline pyrogallate, will remove NO, together with the excess of oxygen used. NO is also readily absorbed by solution of $FeSO_4$.

I. Marsh gas and nitrogen are left to be estimated by difference. They may be separated by adding more than double the volume of pure oxygen, measuring the total volume, and passing the mixture into an *explosion pipette* (fig. 55), where it is ignited by an electric spark between two platinum terminals fused into the upper part of E. The marsh gas then forms CO_2 and H_2O, and the resulting gas having been treated in the KHO pipette to remove the CO_2, and then remeasured, $\frac{1}{3}$ of the total loss in volume represents the CH_4 present. Lastly, the excess of O_2 having been removed by alkaline pyrogallate, the remainder is N_2.

f. If the mixture should contain HCl, HBr, HI, SO_2, H_2S, and NH_3, all of which are soluble in water, they are previously dissolved out thereby in a special apparatus (fig. 56), and the solution so obtained is treated by methods of gravimetric and ordinary volumetric analysis.

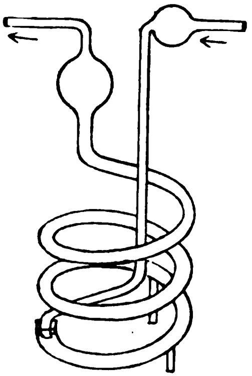


Fig. 56.

Full details of the analysis of gases, beyond the scope of the present work, will be found in Sutton's "Volumetric Analysis."

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